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Transactions

of the

ASME

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I—Introductory Comments to a Series of Contributions on Gas Properties

By F. G. KEYES,[1] CAMBRIDGE, MASS.

The symposium of which this comment serves as an introduction is the result of a meeting in April, 1947, of the ASME Special Research Committee on Properties of Gases, at which it was decided to review the present available knowledge of the properties of twelve gases and to plan a program of investigations to amplify this knowledge to meet present-day application requirements. The twelve pure substances are helium, argon, mercury, hydrogen, nitrogen, oxygen, carbon monoxide, water, carbon dioxide, ammonia, methane, and ethylene, to which the natural mixture air has been added because of its general importance.

The gas properties of immediate interest in the present survey, as designated by the Committee, are the pressure-volume-temperature relation, specific heat, enthalpy (H), equilibrium constants for common reactions, and derived quantities, such as, entropy (S), and free energy (F), or the function[2] $F = H - TS$, where T is the temperature. In addition, the following nonthermodynamic properties are included: Heat conductivity, viscosity, diffusivity, emissivity, and sound velocity.

In view of the extended nature of the assignment, coupled with the fact that other members of the Committee are actively contributing new information in the field of gas properties, the collaboration of six colleagues was requested. The complete list of contributors to the presentation of gas properties follows:

Mr. Serge Gratch, department of mechanical engineering, Towne Scientific School, University of Pennsylvania: "The Vapor Pressure and p-v-T Data for He, A, Hg, H_2, N_2, O_2, CO, CO_2, Air."

Prof. George A. Hawkins, department of mechanical engineering, Purdue University: "A Brief Review of Available Data on Dynamic Viscosity and Thermal Conductivity for Twelve Gases."

Prof. Gerhard Herzberg, Yerkes Observatory, University of Chicago: "Molecular Constants From Spectroscopic Data."

Prof. H. L. Johnston, department of chemistry, Ohio State University: "Joule-Thomson Coefficients and Enthalpy Data."

Prof. Frederick G. Keyes, department of chemistry, Massachusetts Institute of Technology: "Vapor Pressure, Specific Volume and p-v-T Data for H_2O, NH_3, CH_4, C_2H_4."

Dr. John G. Miller, department of chemistry and chemical engineering, University of Pennsylvania: "Dielectric Constants and Refractivity Data."

Dr. Frederick G. Rossini, National Bureau of Standards: "Heats of Formation and Chemical Thermodynamic Properties."

Purpose of Survey

The general purpose of the survey is to review the state of present available knowledge of the properties of the twelve gases selected, and on the basis of this evaluation ultimately to map a series of investigations designed to complete our knowledge to a sufficient degree for the solution of problems of design and operation of gas turbines and rocket motors, as well as to solve the situations arising in combustion processes, flow problems, and heat transmission.

During the past 30 years there has been an accelerated output of accurate pressure-volume-temperature data for a wide range of substances. However, in the past, the demand for this information has greatly exceeded the supply in several directions, and now accurate information is needed at higher temperatures than are readily accessible to the early techniques of measurement. Thus the upper limit of the steam investigations, sponsored by this Society beginning in the early 1920's, reached a temperature of 860 F, which exceeds the temperature of accurate measurement of volume and pressure for any substance. At present, however, reliable data are desired for some engineering projects to temperatures of at least 1500 F, and even higher in the case of some substances.

It is believed that accurate data can be secured at these temperatures but, as already indicated, not by the use of the older methods above 900 F. To obtain the new information, use can be made of flow methods for the measurement of enthalpy changes with pressure, methods which had been under development for some time prior to 1940.

Information about the zero-pressure specific heats of gases of simpler composition, i. e., hydrogen, nitrogen, oxygen, carbon monoxide, can be computed satisfactorily from fundamental molecular constants obtained from the mutual relations of the spectral lines of the substances leading to the energy levels of the molecule. From these levels the zero-pressure specific heats can be computed accurately to very high temperatures, indeed with precision to several thousand degrees Centigrade. In the case of triatomic molecules, the spectral data are less easy to obtain and more difficult to interpret, while the molecules of greater complexity offer correspondingly greater difficulties. In his paper, Professor Herzberg will give a clear impression of these details of a development which has made great strides in the past 20 years.

Wide Range of Information Required

A great deal of exact information at atmospheric pressure is

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[1] Department of Chemistry, Massachusetts Institute of Technology.

[2] These quantities by implication suggest the problem of the equation of state or the correlation of the p-v-T data. The very considerable practical importance of discovering an accurate analytical form or forms for the purpose should provide the subject matter of a special communication, in view of the existing partial theoretical basis which now exists not only for the equation of state for pure gases but also for mixtures. An excellent summary of the status of the problem was presented some years ago by J. A. Beattie and W. H. Stockmayer.[3]

[3] "Equations of State," by J. A. Beattie and W. H. Stockmayer, Reports on Progress in Physics, vol. 7, 1940, p. 195.

Contributed by the Applied Mechanics and Heat Transfer Divisions, under the auspices of the Research Committee on Properties of Gases and Gas Mixtures, and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-161.

lacking regarding heat conductivities, viscosities, and diffusivities, fundamentally transport phenomena, of energy, of momentum, and of mass. The pressure effects are but little known, and without increased knowledge, generally, the solution of flow and heat-transmission problems is much hampered.

The measurement of radiation coefficients should also receive early attention, since exchange of energy by radiation takes on increasing significance as higher temperatures are encountered. Parallel with the investigation of radiation coefficients, it would be desirable to investigate the causes of the change of the coefficients under various circumstances.

The analytical correlation of data on properties is very important since a reliable and accurate correlative relationship reduces enormously the amount of experimental material requi For example, the development of the theory of intermolecu force has led to an understanding of the first-order departur gases from the ideal gas law relating pressure, volume, and t perature, not only for pure substances but with important plications with respect to mixtures. An example will be gi in the course of the present series of papers of the fidelity w which p-v-T data may be correlated.

A great deal remains to be discovered empirically about correlation of the pressure and temperature effects for visco and heat conduction. To date a considerable basis exists for temperature effect at low pressures, but little for the combi effects of pressure and temperature.

II—Molecular Constants From Spectroscopic Data

By G. HERZBERG,[1] WILLIAMS BAY, WIS.

A brief discussion is given of how from the study of molecular spectra those molecular constants can be obtained that are of importance for the calculation of thermodynamic functions of gases in the ideal gaseous state. Subsequently, the existing data are reviewed for the specific gases at present under consideration by the ASME Special Research Committee on Properties of Gases.

THE zero-pressure thermodynamic properties of gases can be derived from a knowledge of the energy levels of the corresponding molecules. These energy levels can be obtained directly from the spectra of the molecules considered. Once their positions have been established, it is a matter of simple, though lengthy, calculations to predict with complete certainty and high accuracy the zero-pressure specific heat, enthalpy, and reduced entropy of the gas under consideration.

There are essentially three contributions to the energy of a molecule: namely, 1, that resulting from the motion of the electrons; 2, that due to the vibrations of the nuclei; and 3, that resulting from the rotation of the whole molecule (or in some cases of its parts with respect to one another). The electronic energy is entirely similar to that for atoms. It gives the largest contribution to the energy. Frequently, except at very high temperatures, only the electronic ground state need be considered in calculations of thermodynamic functions. In each electronic state the molecule may have various (discrete) amounts of vibrational energy, and in each vibrational level it may have various (discrete) amounts of rotational energy. The vibrational and rotational energy levels are the most important for the calculation of thermodynamic functions.

For a diatomic molecule the vibrational-energy levels are given by (in cm^{-1})

$$G(v) = \omega_e(v + {}^1/_2) - \omega_e x_e(v + {}^1/_2)^2 + \ldots .$$

where v is the vibrational quantum number which can assume the values 0, 1, 2, . . . and where ω_e is the (classical) vibrational frequency for infinitesimal amplitudes and $\omega_e x_e$ $(<<\omega_e)$ a constant indicating the anharmonicity of the vibrations. For polyatomic molecules there are several "normal" vibrations of frequency ω_i and quantum number v_i, and the vibrational energy is

$$G(v_1, v_2, v_3, \ldots) = \Sigma\omega_i\,(v_i + {}^1/_2) + \Sigma\Sigma\, x_{ik}\,(v_i + {}^1/_2)\,(v_k + {}^1/_2) + \ldots$$

where the x_{ik} are small anharmonicity constants.

The rotational levels of a diatomic molecule are given in the simplest case by

$$F(J) = B_v J(J + 1)$$

where J is the rotational quantum number and B_v is a constant slightly different for different vibrational levels of the same electronic state

$$B_v = B_e - \alpha_e(v + {}^1/_2) + \ldots$$

Here

$$B_e = \frac{h}{4\pi^2 c I_e}$$

where I_e is the moment of inertia of the molecule in the equilibrium position and α_e is small compared to B_e and indicates the interaction of vibration and rotation. For polyatomic molecules there are, in general, three moments of inertia about the three principal axes and the energy levels depend on their values in a manner similar to but more complicated than for diatomic molecules.

The spectra of molecules correspond to transitions between these energy levels. The transitions between different vibrational levels give rise to "bands" each of which has a fine structure which is determined by the different possible transitions between the various rotational levels belonging to the two given vibrational levels. Broadly speaking, it may be said that the separations of bands give the separations of the vibrational levels and therefore the vibrational constants ω_e and $\omega_e x_e$, or ω_i and x_{ik}. Similarly, the separations of appropriate fine structure lines give the separations of the rotational levels and therefore the rotational constants B_e and α_e or the moments of inertia of the molecule.

If the vibrational energy is increased more and more, a point is reached eventually at which the particular bond is broken and the molecule is dissociated. The dissociation energy in the case of diatomic molecules corresponds to the maximum of the function $G(v)$. The dissociation energy can also be determined from the spectrum of the molecule considered. However, this often requires a more detailed investigation of the spectrum than is necessary for the determination of the rotational and vibrational constants. A knowledge of the dissociation energies is necessary in addition to the knowledge of the thermodynamic functions if the equilibrium of gas reactions is to be predicted, particularly the equilibrium concentrations of free atoms and radicals in molecular gases at high temperatures.

With regard to the gases at present under consideration by the ASME Research Committee, the following remarks pertaining to their molecular constants may be made:

For the monatomic gases and vapors He, A, and Hg, the energy levels are so accurately known from the spectrum that the thermodynamic functions can be calculated with an accuracy which is limited only by the accuracy of the fundamental constants.

In the case of the diatomic molecules H_2, O_2, N_2, and CO, the rotational and vibrational constants are known with sufficient accuracy (1)[2] to obtain the thermodynamic functions with an accuracy of 0.1 per cent or better to fairly high temperatures. For all four molecules, further improvements of the molecular constants are possible and desirable for the calculation of the

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Contributed by the Applied Mechanics and Heat Transfer Divisions, under the auspices of the Research Committee on Properties of Gases and Gas Mixtures, and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society.

[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

thermodynamic functions at very high temperatures. In the case of O_2, the rotational constants recently have been determined with a much improved accuracy by Babcock and Herzberg (2). Moreover, O_2 is the only molecule of those being considered in this paper, for which excited electronic states become of importance for the calculation of thermodynamic functions at high temperatures. Precise data for these excited electronic states of O_2 have recently been determined at Yerkes Observatory (2, 3).

The outstanding problem is the question of the dissociation energies of N_2 and CO. These are of importance not only for the calculation of equilibria of gas reactions but also for the determination of the atomic heats of formation of many polyatomic molecules, the heat of sublimation of carbon, and other problems. For the dissociation energies of both N_2 and CO, several conflicting values appear in the literature, between which, as yet, no unambiguous decision has been obtained. In the case of N_2 some unpublished work of L. Herzberg strongly supports the value of 7.384 first given by Herzberg and Sponer (4). Work aimed at a decision of the question of the heat of dissociation of CO is in progress at Yerkes Observatory.

For the polyatomic molecules CO_2, H_2O, NH_3, CH_4, and C_2H_4 the rotational and vibrational constants as yet are not known with as high a precision as those of the diatomic molecules just discussed. Nevertheless, except for the case of C_2H_4 for which there is still an uncertainty about the identification of two of the normal vibrations, the available spectroscopic data (5) are sufficient to calculate thermodynamic functions up to 1000 deg K with an accuracy of, say, 5 per cent. Most of the uncertainty results from the inaccuracy of the anharmonic constants x_{ik} thus far available. This inaccuracy will have an even larger effect at still higher temperatures. Work is in progress in this laboratory on the higher vibrational levels of CO_2 and CH_4, which it is hoped will lead to more precise values for the anharmonic constants. Several laboratories are engaged in a further study of the vibrations of the C_2H_4 molecule.

The values of the rotational constants B_e and α_e have only a very slight effect on heat capacity and heat content, but do affect appreciably entropy and free energy. As an illustration, the effect of the discrepancy between two recently published values of the rotational constant B_0 of CO_2 may be mentioned. The author (5) some time ago derived a value of 0.3895 cm^{-1} for this constant from measurements of Barker and Adel (6), and Cameron and H. H. Nielsen (7), while more recently A. H. Nielsen and Yao (8) obtained a value of 0.3910 from new measurements of the infrared band at 4.25 μ. Depending upon which value is chosen, entropy values differing by 0.0076 cal/mole/deg are obtained. Very recently a more accurate B value, 0.39043, has been determined by the author from photographic infrared bands. With this value, the error in the contribution to the entropy should be less than 0.002 cal/mole/deg.

There is no question but that an intensive study of the spectra of CO_2, H_2O, NH_3, CH_4, and C_2H_4 will make it possible to derive molecular constants and therefore thermodynamic functions of these molecules comparable in accuracy to those now available for the diatomic molecules discussed in this paper.

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III—Heats of Formation and Chemical Thermodynamic Properties

By FREDERICK D. ROSSINI,[1] WASHINGTON, D. C.

This report describes the tables of selected values of chemical thermodynamic properties issued by the National Bureau of Standards and presents a summary of values of the heats of formation of the molecules H_2O, CO, CO_2, CH_4, C_2H_4, NH_3, and the atoms O, H, N, C, all in the gaseous state.

INTRODUCTION

THE assembly of the table of values of the heats of formation in the International Critical Tables (1),[2] published in 1929, was the first attempt ever made to collate all the published data involving heats of reaction, and to prepare therefrom a self-consistent table of selected values of the heats of formation of the chemical substances. A revision and extension of these tables was published in 1936, in book form (2). However, it became obvious that the continuous maintenance of a complete thermochemical table is a work too great to be borne by individuals through part-time work as an "extracurricular" activity.

NBS TABLES OF CHEMICAL THERMODYNAMIC PROPERTIES

In 1940 the National Bureau of Standards officially undertook the responsibility of maintaining tables of thermochemical and other chemical thermodynamic data by assigning one investigator to work full time on this project under the direction of the author in the NBS Section on Thermochemistry and Hydrocarbons. Since then, the full-time workers on this project have been increased to four, and the first lot of tables was issued as of March 31, 1947. The U.S. Office of Naval Research added its material support to this project beginning January 1, 1947.

The NBS tables of chemical thermodynamic properties are being issued in loose-leaf form in three series, as follows:

In Series I, for all the chemical compounds for which necessary data are available, selected values are given of the following properties:

(*a*) $\Delta Hf^\circ_{298.16}$, the heat of formation at 298.16 deg K (25 deg C), from the elements in their standard states.

(*b*) $\Delta Ff^\circ_{298.16}$, the free energy of formation at 298.16 deg K (25 deg C), from the elements in their standard states.

(*c*) $\log_{10} Kf_{298.16}$, the logarithm of the equilibrium constant of formation at 298.16 deg K (25 deg C), from the elements in their standard states.

(*d*) $S^\circ_{298.16}$, the entropy at 298.16 deg K (25 deg C), for the standard state.

(*e*) $C^\circ_{p\,298.16}$, the heat capacity at 298.16 deg K (25 deg C), for the standard state.

(*f*) ΔHf°_0, the heat of formation at 0 deg K, from the elements in their standard states.

In the tables of Series I, the compounds are arranged in groups according to a standard order. Fig. 1 shows a reproduction of Table 8-1 of Series I, covering certain compounds of the hydrogen group.

In Series II, for all the chemical compounds for which necessary data are available, selected values are given of the following properties:

(*a*) The temperature, heat, and entropy of transition (from one crystalline form to another).

(*b*) The temperature, heat, and entropy of fusion.

(*c*) The temperature, heat, and entropy of vaporization.

Also, in the tables of Series II are included, as appropriate and known, values of the corresponding pressures. The order of arrangement of the substances in Series II is the same as in Series I. Fig. 2 shows a reproduction of Table 10 of Series II, covering certain compounds of the chlorine group.

In Series III, for individual compounds as known or calculable, from 0 deg K to high temperatures (in some cases to 5000 deg K), selected values are given of the following properties:

(*a*) ΔHf°_T, the heat of formation at the given temperature, from the elements in their standard states.

(*b*) ΔFf°_T, the free energy of formation at the given temperature, from the elements in their standard states.

(*c*) $\log_{10} Kf_T$, the logarithm of the equilibrium constant of formation at the given temperature, from the elements in their standard states.

(*d*) $(F^\circ_T - H^\circ_0)/T$, the free energy function at the given temperature, for the standard state.

(*e*) $(H^\circ_T - H^\circ_0)/T$, the heat content (enthalpy) function at the given temperature, for the standard state.

(*f*) S°_T, the entropy at the given temperature, for the standard state.

(*g*) $H^\circ_T - H^\circ_0$, the heat content (enthalpy) at the given temperature, referred to 0 deg K, for the standard state.

(*h*) C°_p, the heat capacity at the given temperature, for the standard state.

In Series III, only one compound is covered in each table. Fig. 3 shows a reproduction of the table of Series III giving values for carbon monoxide.

One set of these tables, with supplements as issued, is being made available to each university department of physics, chemistry, or engineering. U. S. Government laboratories, research institutions, and industrial laboratories may obtain one set each upon request to the National Bureau of Standards. It is planned to have new tables in one or more of the three series issued each quarter. Complete sets of references to the data from which the selected values have been obtained will be issued later.

UNIT OF ENERGY

Calorimetric measurements of energy in the United States have been based on the international joule as derived from mean solar seconds, and the units of international ohms and international

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[1] Chief, Section on Thermochemistry and Hydrocarbons, National Bureau of Standards.

[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

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NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-163.

Series I . Table 8-1 — Hydrogen (at. no., 1; at. wt., 1.0080)

Substance			ΔHf°_0	ΔHf°	ΔFf°	$Log_{10}Kf$	S°	C_p°
			At 0 °K	At 298.16 °K (25 °C)				
Formula	Description	State	kcal/mole	kcal/mole	kcal/mole		cal/deg mole	cal/deg mole
H	1s ($^2S_{1/2}$)	g	51.620	52.089	48.575	-35.60481	27.393	4.968
H^+		g	365.133	367.083				
H^+	std.state, hyp.m=1	aq		0.000	0.000	0.00000	0.000	0.000
H_2		g	0.000	0.000	0.000	0.00000	31.211	6.892
H_2		aq						
OH		g	10.0	10.06	8.93	-6.546	43.888	7.141
OH^-		g	-75.	-76.4				
OH^-	std.state, hyp.m=1	aq		-54.957	-37.595	27.5567	-2.519	-32.0
H_2O	water	g	-57.1043	-57.7979	-54.6351	40.04695	45.106	8.025
		liq		-68.3174	-56.6899	41.55301	16.716	17.996
H_2O_2		g		-31.83				
		liq		-44.84				
	std.state, hyp.m=1	aq		-45.68				
	in 1 H_2O	aq		-45.43				
	2 H_2O	aq		-45.55				
	3 H_2O	aq		-45.60				
	5 H_2O	aq		-45.64				

National Bureau of Standards, Washington, D.C. March 31, 1947; June 30, 1947

Fig. 1 Selected Values of Chemical Thermodynamic Properties for Hydrogen Compounds

Series II Table 10 — Chlorine (at. no., 17; at. wt., 35.457)

Substance		Process			Pressure	Temperature		ΔH	ΔS	ΔC_p
Formula	Description	Type	Initial State	Final State	mm Hg	°C	°K	kcal/mole	cal/deg mole	cal/deg mole
Cl_2		Fusion	c	liq		-100.98	172.18	1.531	8.892	2.75
		Vaporization	liq	g		-100.98	172.18			
		Vaporization	liq	g	760	-34.05	239.11	4.878	20.40	-8.76
ClO_2		Vaporization	liq	g	760	11	284	7.13	25.1	
Cl_2O		Vaporization	liq	g	760	1.9	275.1	6.11	22.2	
Cl_2O_7		Vaporization	liq	g	85.31	25.00	298.16	7.96	26.7	
		Vaporization	liq	g	760	81.5	354.7	7.88	22.2	
HCl		Transition	c, II	c, I		-174.74	98.42	0.2843	2.889	1.15
		Fusion	c, I	liq		-114.19	158.97	0.4760	2.994	2.10
		Vaporization	liq	g	760	-85.03	188.13	3.86	20.5	-7.14
$HCl \cdot 2H_2O$		Fusion	c	liq	760	-18	258	2.5	9.7	
ClF		Vaporization	liq	g	760	-100.3	172.9	5.34	30.88	
ClF_3		Vaporization	liq	g	760	11.4	284.6	5.74	20.2	
ClO_2F		Vaporization	liq	g	760	-5.8	267.4	5.60	20.9	

National Bureau of Standards, Washington, D.C. June 30, 1947

Fig. 2 Selected Values of Chemical Thermodynamic Properties for Chlorine Compounds

Series III. **Table** 23 .— Carbon compounds.

Substance – CO (g); mol. wt., 28.010.

Property	**Units**	**Temperature in °K**									
		0	**50**	**100**	**150**	**200**	**250**	**298.16**	**300**	**400**	**500**
ΔHf°	kcal/mole	-27.2019				-26.5967	-26.4933	-26.4157	-26.4131	-26.317	-26.295
ΔFf°	kcal/mole	-27.2019				-30.7342	-31.7819	-32.8079	-32.8464	-35.007	-37.184
$\mathrm{Log}_{10}\,Kf$						33.58452	27.78357	24.04778	23.92832	19.12679	16.25296
$(F^\circ-H_0^\circ)/T$	cal/deg mole	0				-37.574	-39.124	-40.350	-40.391	-42.393	-43.947
$(H^\circ-H_0^\circ)/T$	cal/deg mole	0				6.9470	6.9495	6.9514	6.9515	6.9594	6.9799
S°	cal/deg mole	0				44.521	46.074	47.301	47.342	49.352	50.927
$H^\circ-H_0^\circ$	cal/mole	0				1389.40	1737.38	2072.63	2085.45	2783.8	3490.0
C_p°	cal/deg mole	0				6.956	6.958	6.965	6.965	7.013	7.120

		600	**700**	**800**	**900**	**1000**	**1100**	**1200**	**1300**	**1400**	**1500**
ΔHf°	kcal/mole	-26.330	-26.407	-26.511	-26.635	-26.768	-26.909	-27.056	-27.212	-27.376	-27.545
ΔFf°	kcal/mole	-39.358	-41.526	-43.677	-45.816	-47.942	-50.053	-52.153	-54.235	-56.308	-58.370
$\mathrm{Log}_{10}\,Kf$		14.33598	12.96488	11.93188	11.12555	10.47761	9.94451	9.49827	9.11764	8.78999	8.50442
$(F^\circ-H_0^\circ)/T$	cal/deg mole	-45.222	-46.308	-47.254	-48.097	-48.860	-49.554	-50.196	-50.789	-51.345	-51.864
$(H^\circ-H_0^\circ)/T$	cal/deg mole	7.0159	7.0654	7.1247	7.1895	7.2565	7.3238	7.3898	7.4538	7.5149	7.5725
S°	cal/deg mole	52.238	53.373	54.379	55.287	56.116	56.878	57.586	58.243	58.860	59.436
$H^\circ-H_0^\circ$	cal/mole	4209.5	4945.8	5699.8	6470.6	7256.5	8056.2	8867.8	9689.9	10520.9	11358.8
C_p°	cal/deg mole	7.276	7.451	7.624	7.787	7.932	8.058	8.167	8.265	8.349	8.419

National Bureau of Standards, Washington, D.C. March 31, 1947

FIG. 3 SELECTED VALUES OF CHEMICAL THERMODYNAMIC PROPERTIES FOR CARBON MONOXIDE

volts, in terms of which certification of standard cells and standard resistances has been made by the National Bureau of Standards. Beginning January 1, 1948, certification of standard cells and resistances by the National Bureau of Standards has been made in terms of absolute volts and absolute ohms. Measurements of power made with apparatus so calibrated will be in terms of absolute watts, with the energy in absolute joules. At the present time, the National Bureau of Standards values for the absolute and international electrical units are such that (33)

1 international joule = 1.000165 absolute joules. . . . [1]

For purposes of tabulation, and for more popular use, it has been found convenient to retain the calorie as the name of a unit of energy. Values of energy actually measured in international joules have been converted to a conventional thermochemical calorie defined by the relation (3, 4)

4.1833 international joules = 1 thermochemical calorie. . [2]

With electrical energy being measured in terms of absolute units, beginning January 1, 1948, the thermochemical calorie may be defined as follows[3]

4.1840 absolute joules = 1 thermochemical calorie. . [3]

Values of energy obtained from spectroscopic measurements are based upon "wave numbers," expressed in reciprocal centimeters. Conversion of wave numbers to the conventional thermochemical calorie is made by means of the relation (5, 6)

1 wave number = 2.8585 ± 0.0009 calories. . . . . [4]

In the same set of fundamental constants the gas constant is (6)

$R = 1.98719 \pm 0.00013$ cal/deg mole. . . . . [5]

with the absolute temperature of the ice point being taken as

0 deg C = 273.160 ± 0.010 deg K. . . . . [6]

THERMOCHEMICAL TABLE

The ideal thermochemical table is one which will permit calculation of the heat of every chemical reaction. Obviously, it is impractical to list in a table the heat of every reaction, but the same end is accomplished by listing for each chemical substance its heat of formation from the elements in selected standard states. It is evident that, by proper selection, the number of chemical reactions whose heats must be determined will be about the same as the number of substances listed in the table. Some saving in the number of reactions to be measured will occur among the organic compounds because of certain simplifying rules for the increment in energy per CH_2 group, and because of certain correlations which may be made in the relation between isomeric structure and energy content (3, 7, 8, 9, 10, 11, 12).

The value of the heat of formation of a given substance may be the result of the determination of the heat of one reaction, as for liquid water and gaseous carbon dioxide

H_2(gas) + $\frac{1}{2}$ O_2 (gas) = H_2O (liquid). . . . . [7]

---

[3] It is important to note that the thermochemical calorie differs from the IT steam calorie by a small amount, as follows:

1 IT steam calorie = $^1/_{860}$ international watt-hour
= 4.18605 international joules
= 1.00065 thermochemical calories

$$C(c,\ graphite) + O_2(gas) = CO_2(gas) \ldots\ldots [8]$$

For many other substances, however, the value will result from the measurement of the heats of a number of chemical reactions. For example, the heat of formation of gaseous methane involves appropriate addition (or subtraction) of three different reactions, including the two foregoing reactions and the following one

$$CH_4(gas) + 2\ O_2(gas) = CO_2(gas) + 2\ H_2O\ (liquid) \ldots [9]$$

From a complete table of heats of formation, the heat of any given reaction is calculated by taking the sum of the heats of formation of the products of the reaction and subtracting the sum of the heats of formation of the reactants.

Heats of Formation of
H_2O, CO, CO_2, CH_4, C_2H_4, NH_3

Selected values of the heats of formation at 298.16 deg K (25 deg C) and 0 deg K, from the elements in their standard reference states, are given for each of these substances in Series I of the NBS Tables of Selected Values of Chemical Thermodynamic Properties, as follows

$$H_2(gas) + {}^1/_2\ O_2\ (gas) = H_2O(gas) \ldots\ldots [10]$$

$$\Delta Hf°_{298.16} = -57.7979 \pm 0.0101\ kcal/mole \ldots [10a]$$

$$\Delta Hf°_0 = -57.1043 \pm 0.0101\ kcal/mole \ldots\ldots [10b]$$

$$C(c,\ graphite) + {}^1/_2\ O_2(gas) = CO\ (gas) \ldots\ldots [11]$$

$$\Delta Hf°_{298.16} = -26.4157 \pm 0.0307\ kcal/mole \ldots [11a]$$

$$\Delta Hf°_0 = -27.2019 \pm 0.0307\ kcal/mole \ldots\ldots [11b]$$

$$C(c,\ graphite) + O_2(gas) = CO_2(gas) \ldots\ldots [12]$$

$$\Delta Hf°_{298.16} = -94.0518 \pm 0.0108\ kcal/mole \ldots\ldots [12a]$$

$$\Delta Hf°_0 = -93.9686 \pm 0.0108\ kcal/mole \ldots\ldots [12b]$$

$$C(c,\ graphite) + 2\ H_2(gas) = CH_4(gas) \ldots\ldots [13]$$

$$\Delta Hf°_{298.16} = -17.889 \pm 0.075\ kcal/mole \ldots\ldots [13a]$$

$$\Delta Hf°_0 = -15.987 \pm 0.075\ kcal/mole \ldots\ldots [13b]$$

$$2\ C(c,\ graphite) + 2\ H_2(gas) = C_2H_4\ (gas) \ldots\ldots [14]$$

$$\Delta Hf°_{298.16} = 12.496 \pm 0.066\ kcal/mole \ldots\ldots [14a]$$

$$\Delta Hf°_0 = 14.522 \pm 0.066\ kcal/mole \ldots\ldots [14b]$$

$${}^1/_2\ N_2\ (gas) + {}^3/_2\ H_2(gas) = NH_3(gas) \ldots\ldots [15]$$

$$\Delta Hf°_{298.16} = -11.04 \pm 0.10\ kcal/mole \ldots\ldots [15a]$$

$$\Delta Hf°_0 = -9.38 \pm 0.10\ kcal/mole \ldots\ldots [15b]$$

The foregoing values of heats of formation are believed to be reliable within the limits of uncertainty indicated (13).

References to the sources of the foregoing values are as follows: H_2O(1, 2, 5, 14); CO (1, 2, 5, 15); CO_2 (1, 2, 17, 18, 19, 20); CH_4 (1, 2, 9, 15); C_2H_4(1, 2, 10, 16); NH_3 (1, 2, 21). Additional references are given in the papers cited.

Heats of Formation of
The Gaseous Atoms O, H, N, C

For convenience, the values of the heats of formation of the gaseous atoms are referred to the elementary molecules of the same substances. The heats of formation of the gaseous atoms of oxygen, hydrogen, and nitrogen are best evaluated from spectroscopic values of the heats of dissociation of the corresponding diatomic elementary molecules into the monatomic atoms, each in the gaseous state in the ground level of energy. With regard to gaseous monatomic carbon, values may be calculated in two ways as follows: One way involves the spectroscopic heat of dissociation of gaseous carbon monoxide (into gaseous monatomic carbon and oxygen) and the heats of formation of monatomic gaseous oxygen and of gaseous carbon monoxide, as follows

$$CO(gas) = C(gas) + O(gas) \ldots\ldots [16]$$

$${}^1/_2\ O_2(gas) = O\ (gas) \ldots\ldots [17]$$

$$C(c,\ graphite) + {}^1/_2\ O_2(gas) = CO(gas) \ldots\ldots [18]$$

The sum of Reactions [16] and [18], less Reaction [17], yields

$$C(c,\ graphite) = C(gas) \ldots\ldots [19]$$

The second way of evaluating the heat of formation of gaseous monatomic carbon is to utilize experimental data on the vapor pressure of graphite as a function of temperature. The heat of sublimation of carbon is related to the change of vapor pressure with temperature by means of the thermodynamic relation

$$\Delta H = T(\Delta V)\ (dP/dT) \ldots\ldots [20]$$

where, for the process of sublimation, ΔH and ΔV are the increments in heat content (enthalpy) and volume, respectively, per mole, P is the pressure, and T is the absolute temperature. In evaluating experimental data of the foregoing kind, appropriate accounting must be made, if significant, of that fraction of gaseous carbon which is diatomic rather than monatomic.

Selected values of the heats of formation at 298.16 deg K (25 deg C) and 0 deg K, from the elements in their standard reference states, are given for gaseous monatomic oxygen, hydrogen, and nitrogen in Series I of the NBS Tables of Selected Values of Chemical Thermodynamic Properties, as follows

$${}^1/_2\ O_2(gas) = O\ (gas) \ldots\ldots [21]$$

$$\Delta Hf°_{298.16} = 59.159 \pm 0.050\ kcal/mole \ldots\ldots [21a]$$

$$\Delta Hf°_0 = 58.586 \pm 0.050\ kcal/mole \ldots\ldots [21b]$$

$${}^1/_2\ H_2(gas) = H(gas) \ldots\ldots [22]$$

$$\Delta Hf°_{298.16} = 52.089 \pm 0.010\ kcal/mole \ldots\ldots [22a]$$

$$\Delta Hf°_0 = 51.620 \pm 0.010\ kcal/mole \ldots\ldots [22b]$$

$${}^1/_2\ N_2(gas) = N(gas) \ldots\ldots [23]$$

$$\Delta Hf°_{298.16} = 85.566 \pm 0.060\ kcal/mole \ldots\ldots [23a]$$

$$\Delta Hf°_0 = 85.120 \pm 0.060\ kcal/mole \ldots\ldots [23b]$$

$$C(c,\ graphite) = C(gas) \ldots\ldots [24]$$

$$\Delta Hf°_{298.16} = 126.362\ or\ 171.698\ kcal/mole \ldots\ldots [24a]$$

$$\Delta Hf°_0 = 125.055\ or\ 170.391\ kcal/mole \ldots\ldots [24b]$$

For the foregoing values, uncertainties are given for the values for gaseous monatomic oxygen, hydrogen, and nitrogen. With regard to the value for gaseous monatomic carbon, the situation is complicated by the fact that the published data are conflicting. For the heat of sublimation of graphite at 0 deg K, the most probable interpretations at the present writing yield two different precise values, one near 125 kcal/mole, and the other, near 170 kcal/mole, as given by Equations [24a] and [24b].

In 1936, at the suggestion of the author, G. Herzberg reviewed (22) the existing spectroscopic data on the energy of dissociation of carbon monoxide, as given by Equation [16]. Herzberg then concluded that, while there were several possible values, the most probable one was that which yielded the value near 125 kcal/mole for the heat of sublimation of graphite at 0 deg K. Subsequently, other reports have appeared, some favoring a lower value (23, 24) and some favoring a higher value (25). In a recent comprehensive review of the entire problem, Long and Norrish (26) conclude that the value recommended in 1936 by Herzberg still appears to be the most probable one. New experimental data which are known to be in progress in several different laboratories should help to settle this important question. In particular, reference may be made to the recent work of Brewer and Gilles who recommend the value near 170 kcal/mole for the heat of sublimation of graphite at 0 deg K.

References to the sources of the values for the heats of formation of the gaseous atoms are as follows: O(27); H(28); N(29, 30, 25); C(22, 23, 24, 25, 26, 31, 32). Additional references are given in the papers cited.

Note added in proof: The new publication of L. Brewer, P. W. Gilles, and F. A. Jenkins, *Journal of Chemical Physics*, vol. 16, 1948, appears definitely to fix the value for the heat of sublimation of graphite at 0 deg K to be the one near 170 kcal/mole.

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IV—Vapor Pressure, Specific Volume, p-v-T Data for H_2, N_2, O_2, CO, CO_2, Air, He, A, Hg

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Accurate p-v-T data are available for the pure gases H_2, N_2, He, and A, from very low temperatures to about 400 C; for O_2 from —152 to 100 C; for CO from —70 to 200 C; for CO_2 from 0 to 150 C; for air from —145 to 200 C. For Hg, p-v-T data are practically nonexistent. With the exception of the systems N_2–H_2 and N_2–CH_4, p-v-T data for mixtures of the gases here considered are quite incomplete and certainly inadequate for accurate practical applications. Adequate vapor-pressure data are available for all the pure gases here considered, but not for their mixtures. The theory of gas properties has been developed sufficiently to be useful for formulation and reasonable extrapolation of existing data; however, present theory is inadequate for reliable a priori calculation of gas properties, except for the simplest molecules.

Introduction

During the last half-century an extremely large amount of accurate p-v-T data for pure gases has been collected. Following the amazingly accurate and extensive researches of Amagat (1, 2)[2] and of his contemporaries, many investigators have contributed experimental information on the p-v-T relations of real gases. The main contributors have been (1) Holborn and co-workers at the Physikalisch-Technische Reichsanstalt; (2) Onnes and co-workers at the University of Leiden; (3) Bartlett and co-workers at the Fixed Nitrogen Laboratory; (4) Keyes and Beattie at M.I.T.; (5) Michels and co-workers at Amsterdam. These investigators have covered adequately the temperature range from the normal boiling point of oxygen to about 400 C in the case of almost all common pure gases. The pressures covered by these investigators, in general, extend to about 100 atm; however, Michels and others have extended the pressure range to 3000 atm in the case of some gases. While the experimental information on pure gases may be considered adequate, in general, data on technically important gas mixtures are scanty or altogether absent.

It is not practical to attempt here a complete critical review of all available gas-compressibility data; however, an attempt will be made to give a general survey sufficiently complete to indicate the ranges of conditions for which sufficient information is available and to point out the main needs for additional research. For this purpose we shall omit mention of the older p-v-T data, which, generally, are not sufficiently accurate on the basis of present standards. Several excellent reviews of the data available before 1930 are available (75, 110, 132); therefore this paper will omit mention of the less important papers published before that date, and will place emphasis on the more recent p-v-T work.

The vapor pressure of the pure gases considered in this report is known with sufficient accuracy for all usual practical applications; however, the liquid-vapor saturation data for mixtures are not known with comparable accuracy and completeness. Probably, with the growing importance of liquefaction methods for gas separation, it will be necessary to obtain additional data on the liquid-vapor equilibrium of some of the more important mixtures. The vapor-pressure data obtained before 1924 have been reviewed and formulated quite adequately by Crommelin in the section of "International Critical Tables" on vapor pressure (29, 64). Therefore this paper will consider only liquid-vapor and solid-vapor equilibrium data obtained since 1924. Unfortunately, this report is not complete in this respect, since some important recent results of Russian determinations of liquid-vapor equilibrium for mixtures are unavailable to the author.

It is interesting to note that vapor pressures, latent heats of evaporation or sublimation, and p-v-T data are interrelated through identical relations of thermodynamics. These relations have been used to obtain vapor pressures from p-v-T data or vice versa (32). Unfortunately, this procedure depends very strongly upon an accurate knowledge of the thermodynamic temperature scale. Experimental measurements are usually made on the international scale; the relation of this to the thermodynamic scale is known quite accurately in the range 0 to 100 C; the accuracy of the knowledge of this relation at very high or very low temperatures is questionable. Therefore very careful gas-thermometry research should be undertaken to minimize this serious source of uncertainty in the correlation of vapor-pressure data with p-v-T data.

The usefulness of the available p-v-T data depends markedly on the reliability of their formulation, since quite often it is necessary to use values of the properties at temperatures higher or lower than those at which the experimental determinations have been carried out; great care is required to make the extrapolation reliable. During the first two decades of this century, compressibility data were usually formulated by means of empirical equations of state. The number of equations of state used is too large to permit a detailed discussion here. The reader is referred to the excellent review by Otto (132) on this subject. Probably the best of the equations of state with a small number of adjustable constants is the Beattie-Bridgeman equation

$$pv = RT\left(1 - \frac{c}{vT^3}\right)\left[1 + \frac{B_0}{v}\left(1 - \frac{b}{v}\right)\right] - \frac{A_0}{v}\left(1 - \frac{a}{v}\right) \ldots [1]$$

where

p = absolute pressure
v = specific volume
R = universal gas constant

---

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[2] Numbers in parentheses refer to the Bibliography at end of paper.

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-164.

T = absolute temperature
c, B_0, b, A_0, a = empirical constants

An excellent survey of the applications of the Beattie-Bridgeman equation has been given by Beattie and Stockmayer (11). Table 1 summarizes the Beattie-Bridgeman constants for the gases considered in this report. Mercury is not included since the available p-v-T data for mercury vapor are insufficient to determine the five Beattie-Bridgeman constants. The constants for N_2 in Table 1 may be used also for CO with fair accuracy. In general, the Beattie-Bridgeman equation fits the experimental data rather well, at least for densities smaller than one half the critical density and pressures lower than 100 atm. In the case of CO_2, however, the deviations of this equation of state from the experimental data are definitely larger than the uncertainty of the data (102).

TABLE 1 CONSTANTS FOR BEATTIE-BRIDGEMAN EQUATION OF STATE (11)

Units: Atm, liter/mole, deg K; R = 0.08206; ice-point temp = 273.13 deg K

Gas	A_0	a	B_0	b	$10^{-4} \times c$	Mol wt
He...	0.0216	0.05984	0.01400	0.0	0.0040	4.00
A....	1.2907	0.02328	0.03931	0.0	5.99	39.91
H_2...	0.1975	—0.00506	0.02096	—0.04359	0.0504	2.0154
N_2...	1.3445	0.02617	0.05046	—0.00691	4.20	28.016
O_2...	1.4911	0.02562	0.04624	0.0004208	4.80	32
Air...	1.3011	0.01931	0.04611	—0.01101	4.34	28.964
CO_2..	5.0065	0.07132	0.10476	0.07235	66.00	44.000

NOTE: The constants in this table are based upon the "International Critical Tables" values of the general physical constants and molecular weights. Revision of this table to agree with the newer values of these constants is not justified, since the changes would be well within the limits of accuracy of the Beattie-Bridgeman equation.

In order to apply the Beattie-Bridgeman equation to gas mixtures, it is necessary to have suitable combination rules for obtaining the constants for the mixtures from those of the constituent gases. Suitable combination rules have been obtained by theoretical considerations and by comparison with experimental data (11, 12, 144). However, these combination rules have not yet been tested widely enough to be considered completely reliable.

As mentioned, the Beattie-Bridgeman equation cannot be used in the case of Hg, since in this case the experimental p-v-T data are not sufficiently extensive and accurate to determine the Beattie-Bridgeman constants. In such a case the only possible procedure consists of using the principle of corresponding states (11, 47); this method is applicable as long as the critical constants are known. Even though this principle does not hold accurately, it may be used with fair reliability if nonpolar gases are treated separately from polar gases (79).

THEORY

During the past three decades great progress has been made in the application of statistical mechanics to the treatment of real ("imperfect") gases. The theory of real gases may be discussed best by writing the equation of state in the virial form

$$pv = RT\left(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \ldots\right) \ldots [2]$$

where $B(T)$, $C(T)$, $D(T)$, ... are pure temperature functions called, respectively, second, third, fourth, ... virial coefficients. It may be shown that these coefficients are related to the intermolecular forces; thus in the case of molecules with a spherically symmetric force field (42, 94)

$$B(T) = 2\pi N \int_0^\infty r^2(1 - e^{-E(r)/kT})dr \ldots\ldots [3]$$

where N is Avogadro's number, k is Boltzman's constant, and $E(r)$ is the intermolecular potential of a pair of molecules separated by a distance r. Mayer and others (94) have obtained general expressions for the relation of all the virial coefficients to the intermolecular potentials.

In order to apply relations of the type of Equation [3] it is necessary to know the intermolecular potential. Only in the case of very few molecules is it practical to calculate $E(r)$ a priori. In general, it is necessary to assume the form of $E(r)$, leaving only few parameters to be adjusted from experimental values of $B(T)$. A satisfactory assumption appears to be the Lennard-Jones potential

$$E(r) = \left(\frac{s}{s-6}\right)\left(\frac{s}{6}\right)^{6/(s-6)} E_m\left[\left(\frac{r_0}{r}\right)^s - \left(\frac{r_0}{r}\right)^6\right] \ldots [4]$$

where E_m, r_0, and s are constants for a given molecule. It is necessary to have $s > 6$; usually it is satisfactory to assume $s = 12$. With this potential it is possible to perform analytically the integration indicated in Equation [3]; the result may be expressed as

$$B(T) = \frac{2}{3}\pi N r^3_0 f_s(y) \ldots\ldots\ldots\ldots [5]$$

where $y = E_m/kT$ and $f_s(y)$ is a relatively simple function of y and of the parameter s. Tables of this function for some values of s are available. This method of formulating second virial coefficients has been applied in the case of most common gases with good success (25, 55, 80). Some modifications are necessary in the case of polar molecules (143, 144), and some refinements are needed in the case of light molecules at very low temperatures (33, 34, 35, 36). In general, this semitheoretical method of formulating second virial coefficients is quite satisfactory and permits a reasonably reliable extrapolation of the experimental data. However, it must be noted that the integral in Equation [3] is relatively insensitive to the exact form of the short-range repulsive forces if the temperature is low; hence good agreement with experimental data at relatively low temperatures does not represent an effective test of the validity of the potential used for small values of r. Since the integral in Equation [3] is more sensitive to the exact value of $E(r)$ for small r at high temperatures, the extrapolation to very high temperatures by the method just outlined is somewhat uncertain. Possibly this state of affairs will be remedied in the future by the determination of the short-range forces by other experimental methods, such as the collision cross-section measurements of Amdur (3, 4).

The theoretical calculation of the third and higher virial coefficients becomes more complicated. Some success has been achieved in the case of the third virial coefficient (27, 94, 109), but the theoretical calculation of higher virial coefficients appears impractical at present. Fortunately, these coefficients decrease in magnitude with increasing temperature; therefore the fact that theory cannot be used at present for the extrapolation of the fourth and higher virial coefficients is not too serious a matter.

It is interesting to note that the theory outlined has been used to relate the Beattie-Bridgeman constants to the intermolecular forces. Thus according to Hirschfelder and Roseveare (55), for molecules satisfying the Lennard-Jones potential with $s = 12$, the following relations hold approximately between the constants in this potential and the Beattie-Bridgeman constants

$$\left.\begin{aligned} E_m &= 0.04127 \times 10^{-15}\,\frac{A}{RB_0}\ \text{ergs} \\ \frac{2}{3}\pi N r_0^3 &= 1.249\ B_0 \\ c &= 0.0236\,\frac{A^3_0}{R^3B_0^2} \end{aligned}\right\} \ldots\ldots [6]$$

Furthermore, Corner (26) states that, for Lennard-Jones molecules, to a close approximation

$$a/B_0 \doteq 0.45; \; b/B_0 = -0.1 \ldots\ldots\ldots\ldots [7]$$

These relations are especially useful to derive combination rules for the Beattie-Bridgeman constants for mixtures, since fairly accurate combination rules for E_m and r_0 may be obtained by theoretical considerations. In order to discuss these combination rules it is necessary to outline the present state of knowledge of the theory of gas mixtures.

Until rather recently almost everybody clung to the belief that the *p-v-T* relations of gaseous mixtures should be related in a very simple way to the *p-v-T* relations of the pure constituents. Results of this faith in the "ultimate simplicity of nature" were Dalton's rule, Amagat's rule, the Lewis-Randall fugacity rule, and several other equally inaccurate conjectures on the relation between the properties of mixtures and the properties of pure gases. More recently, however, some progress has been made toward a more accurate and rational solution of the problem of gaseous mixtures. Thus it has been shown that the second virial coefficient of a gas mixture depends upon the composition in accordance with the equation

$$B = \sum_i \sum_j x_i x_j B_{ij} \ldots\ldots\ldots\ldots [8]$$

where x_i, x_j are mol fractions; the B_{ij}'s for $i = j$ are the second virial coefficients of the pure constituents, while for $i \neq j$ they are interaction coefficients which depend on the force between unlike molecules. On the basis of Equation [3] it is not difficult to obtain rational combination rules for the interaction coefficients in terms of the second virial coefficients for the pure gases. Thus for molecules with spherical symmetry if the Lennard-Jones potential with $s = 12$ is used, so that the potential may be written as

$$E(r) = \frac{\lambda}{r^{12}} - \frac{\mu}{r^6} \ldots\ldots\ldots\ldots [9]$$

then it is possible to obtain the parameters for the interaction coefficients by averaging geometrically μ and averaging arithmetically $r_0 = (\lambda/\mu)^{1/6}$. From these relations and from Equations [6] and [7] it is easy to obtain suitable combination rules for the Beattie-Bridgeman constants for mixtures. By similar methods it is possible to derive rational combination rules in the case of polar molecules (144). For higher virial coefficients, the theoretical treatment is analogous in principle, but of course the actual details of calculation are much more complicated.

Summarizing, the theory of intermolecular forces has been developed sufficiently to permit a rational formulation of the experimental data; unfortunately, in the case of mixtures the available experimental information is meager and therefore the theory of gaseous mixtures has not yet been subjected to sufficiently exhaustive verification to insure its reliability as a predictive tool.

EXPERIMENTAL DATA

(*a*) *Hydrogen.* A summary of the main body of recent *p-v-T* data for hydrogen is given in Table 2.

From an examination of Table 2 it is evident that the *p-v-T* data for H_2 have been determined over a sufficient range of temperature and pressure to allow the derivation of a reliable formulation. The second virial coefficient for H_2 has been formulated by Keyes (80), using practically all the available data, by means of a rational method based on the theory just outlined. Keyes' formulation is

$$B = \tau^{1/4} (60.000 - 380.56\, \tau^{1/2} - 2494.8\, \tau) \text{ (cc per g)}$$

TABLE 2 COMPRESSIBILITY DATA FOR HYDROGEN

Reference	Temp range, deg C	Max press, atm
Leiden isotherms (ref. 31, 37, 113, 114, 120, 121, 122, 123, 125, 126, 127, 128, 130, 134, 137, 148)	—259 to 100	100
PTR isotherms (ref. 49, 52, 57, 59, 61, 62)	—208 to 200	200
Bartlett, et al (ref. 6, 7, 8)	—70 to 400	1000
Basset and Dupinay (ref. 10)	0	5000
Kohnstamm and Walstra (ref. 88, 151)	15.4 and 20	1000
Michels, et al (ref. 99, 100, 104)	0 to 150	3000
Verschoyle (ref. 150)	0 and 20	205
Scott (ref. 149)	25	170
Townend and Bhatt (ref. 147)	0 and 25	600
Johnson[a] (ref. 65)	30	500
Zlunitsyn and Rudenko (ref. 154)	—208 to —182	1000

[a] Johnson obtained at 30 C (with 0.01 per cent consistency) $pv = 24875.08 + 14.822\, p + 0.003553\, p^2$ (cc atm/mole).

where $\tau = 1/T$. Corner (27) has determined the constants in the Lennard-Jones potential to fit the second as well as the third virial coefficient of H_2. De Boer and Michels (33, 34, 35) have calculated the second virial coefficients of H_2 and D_2 using more accurate expressions for the potential, obtaining good agreement with the experimental data.

The normal boiling point of H_2 is 20.39 deg K (22, 50, 53, 56, 64, 71). The triple point of H_2 is 13.96 deg K (56), and the triple-point pressure is 53.85 mm Hg (92). The vapor pressure of H_2 in the range 14 to 21 deg K, according to Henning and Otto (50), is given by

$$\log_{10} p_{mm} = 4.80204 + 0.0167335\, T - \frac{46.1045}{T}$$

where p_{mm} is the vapor pressure in mm Hg, and T is the absolute temperature in deg K (with ice-point temperature 273.16 deg K). The critical constants of H_2 are (64)

t_c = —239.9 deg C
p_c = 12.8 atm
d_c = 0.0310 g per cc

(*b*) *Nitrogen.* A summary of the main body of recent *p-v-T* data for nitrogen is given in Table 3.

TABLE 3 COMPRESSIBILITY DATA FOR NITROGEN

Reference	Temp range, deg C	Max press, atm
Leiden isotherms (ref. 131)	—146 to 20	60
PTR isotherms (ref. 49, 51, 52, 59, 60)	—130 to 400	200
Bartlett, et al (ref. 6, 7, 8)	—70 to 400	1000
Basset and Dupinay (ref. 10)	0	5000
Benedict (ref. 13)	—183 to 200	5800
Keyes and Burks (ref. 81)	0 to 200	300
Michels, et al (ref. 107, 108, 133)	0 to 150	3000
Smith and Taylor (ref. 141, 142)	0 to 200	300
Verschoyle (ref. 150)	0 and 20	205

The *p-v-T* data for N_2 have been determined accurately from —183 to 400 C. The pressure range covered is extremely wide. Noteworthy are the measurements of Benedict (13) which extend over a very wide temperature range with extremely high pressures. Keyes (80) has formulated the second virial coefficient of N_2 in a manner similar to the one used for the H_2 formulation, obtaining

$$B = \tau^{1/4} (10.08 - 766.115\, \tau^{3/4} - 1.7545 \times 10^8\, \tau^{15/4}) \text{ (cc per g)}$$

Corner (25, 27) has determined the constants in the Lennard-Jones potential to fit the second and third virial coefficients of N_2.

The normal boiling point of N_2 in 77.36 deg K (70, 56, 50). The vapor pressure of liquid and solid N_2 has been determined and formulated differently by several investigators (39, 70, 82, 83). Probably the Leiden formulation (70) is the most accurate. The triple point of N_2 is 63.15 deg K (70) and the triple point pressure is 94.0 mm Hg (70, 83). The critical constants of N_2 are (64)

$$\begin{aligned} t_c &= -147.1 \text{ deg C} \\ p_c &= 33.5 \text{ atm} \\ d_c &= 0.311 \text{ g per cc} \end{aligned}$$

(*c*) *Oxygen.* A summary of the main body of recent *p-v-T* data for oxygen is given in Table 4.

TABLE 4 COMPRESSIBILITY DATA FOR OXYGEN

Reference	Temp range, deg C	Max press, atm
Leiden isotherms (ref. 89, 111, 129, 149)	—152 to 20	60
PTR isotherms (ref. 51, 58)	0 to 100	100
Masson and Dolley (ref. 92)	25	125

Since the Leiden isotherms below 0 deg C cover only the range to 9 atm, the *p-v-T* data for O_2 may be considered adequate only for the temperature range from 0 to 100 C. Probably the most reliable available formulation of the second and third virial coefficients of O_2 is the one obtained by Corner (27), using the Lennard-Jones form of the intermolecular potential. This formulation, however, cannot be considered sufficiently reliable because of the inadequacy of the experimental data.

The normal boiling point of O_2 is 90.19 deg K (43, 56, 72, 76). The main recent determination of the vapor pressure of O_2 is that of Dodge and Davis (39). The vapor pressure of O_2 in the range 66–90 deg K is represented adequately by their Equation [50]

$$\log_{10} p_{mm} = 7.86224 - 0.0049832\, T - \frac{408.740}{T}$$

with the same units as in the corresponding equation quoted for H_2. The triple point of O_2 is 54.33 deg K (56). The critical constants are (64)

$$\begin{aligned} t_c &= -118.8 \text{ deg C} \\ p_c &= 49.7 \text{ atm} \\ d_c &= 0.430 \text{ g per cc} \end{aligned}$$

(*d*) *Carbon Monoxide.* The relatively meager *p-v-T* data for carbon monoxide are summarized in Table 5.

TABLE 5 COMPRESSIBILITY DATA FOR CARBON MONOXIDE

Reference	Temp range, deg C	Max press, atm
Goig Botella (ref. 18)	0 to 20	130
Scott (ref. 140)	25	170
Townend and Bhatt (ref. 147)	0 and 25	600
Bartlett, et al (ref. 9)	—70 to 200	1000

The available *p-v-T* data for CO are almost identical with the corresponding data for N_2; therefore usually the equation of state for N_2 is used also for calculations for CO.

The main determination of the vapor pressure of CO is that of Crommelin et al (30). The normal boiling point of CO is 81.6 deg K (30, 56); the triple point is 68.1 deg K (30, 56); the triple-point pressure is 0.15146 atm. The critical constants are (93)

$$\begin{aligned} t_c &= -140.2 \text{ deg C} \\ p_c &= 34.53 \text{ atm} \\ d_c &= 0.3010 \text{ g per cc} \end{aligned}$$

(*e*) *Carbon Dioxide.* The main body of *p-v-T* data for CO_2 has been obtained by A. Michels, et al (97, 98, 101, 102, 103, 116), who have also determined the melting curve of this substance, as well as several other properties. The only other significant *p-v-T* data for CO_2 are the famous but relatively inaccurate data of Amagat (2), those of Lowry and Erickson (90), and those of Keesom in the neighborhood of the critical point (67). The Michels *p-v-T* data cover the range from 0 to 150 C up to pressures of 3000 atm. Below 1000 atm, the Michels' data are probably accurate to 0.02 per cent. Although these data are extremely accurate, they do not cover a sufficient range of temperatures to allow the derivation of a reliable equation of state. Probably the best formulation is the one given by Corner (27). The formulation used by Corner takes into account the fact that the symmetry of the force field surrounding a CO_2 molecule is more nearly cylindrical than spherical. The author, however, believes that Corner's formulation cannot be considered definitive, since it is based upon data which cover only a very narrow temperature range. Sweigert's method of extrapolation of the experimental CO_2 data is even less reliable, since Sweigert (145) uses for this purpose the principle of corresponding states, which cannot be expected to be followed closely by CO_2, because of the marked difference between this molecule and most other nonpolar molecules.

The vapor pressure of liquid and solid CO_2 have been determined quite accurately by many investigators. It will suffice here to mention the measurements of Bridgeman (19), of Giauque and Egan (45), of Heuse and Otto (53, 54), and of Meyers and van Dusen (96). A more complete bibliography is given by Meyers and van Dusen (96), who have formulated all the vapor-pressure data obtained before 1933; the Meyers and van Dusen formulation is undoubtedly the best available. The normal sublimation point of CO_2 has been investigated quite extensively as a possible thermometric fixed point. The best value is probably —78.514 C on the international scale (96, 54, 53, 45); some discrepancies in reported values of the normal sublimation point of CO_2 may be due to a slight difference between the thermodynamic and the international temperature scales, a difference which is usually ignored. The triple point of CO_2 is at —56.602 C, 3885.2 mm Hg (96). The critical constants of CO_2 are (98, 24)

$$\begin{aligned} t_c &= 31.04 \text{ deg C} \\ p_c &= 72.85 \text{ atm} \\ d_c &= 0.467 \text{ g per cc} \end{aligned}$$

(*f*) *Air.* The most important *p-v-T* data for air are summarized in Table 6.

TABLE 6 COMPRESSIBILITY DATA FOR AIR

Reference	Temp range, deg C	Max press, atm
Leiden isochores (ref. 135)	—145 to 20	60
PTR isotherms (ref. 63)	0 to 200	100
Burnett (ref. 21)	30	60

It is clear that the *p-v-T* data for air are not quite adequate, since they cover only the range —145 to 200 C at moderate pressures.

Since air is a mixture of several gases (mainly nitrogen, oxygen, and argon), the determination of the liquid-vapor equilibrium consists of the measurement of the composition of the vapor in equilibrium with liquid of given composition as a function of the temperature or of the pressure. In addition, the saturation pressure must be determined as a function of the liquid or vapor composition and of the temperature. The main measurements of the liquid-vapor equilibrium for this system have been carried out by Dodge and Dunbar (40), who covered the range —196 to —148 C.

(*g*) *Helium.* The compressibility of helium has been measured over an extremely wide temperature range by a large number of investigators. An excellent review of the available data for this substance has been given by Keesom (69). A partial list of reference on the *p-v-T* data for helium is given in Table 7.

The experimental coverage of the *p-v-T* data for helium is excellent, and the theoretical study of the properties of this gas has been carried out very thoroughly. Probably the best theo-

TABLE 7 COMPRESSIBILITY DATA FOR HELIUM

Reference	Temp range, deg C	Max press, atm
Leiden isotherms (ref. 17, 73, 77, 78, 85, 112, 115, 117, 118, 119, 136, 148)	—271.5 to 100	60
PTR isotherms (ref. 49, 51, 52, 58, 59, 60, 62, 63)	—258 to 400	200
Michels and Wouters (ref. 106)	0 to 150	300
Buchmann (ref. 20)	—260 to —253	2000
Burnett (ref. 21)	0 and 50	114
Gibby, Tanner, Masson (ref. 46)	25 to 175	125
Wiebe, Gaddy, Heins (ref. 153)	—70 to 200	1000
Johnson[a] (ref. 65)	30	500

[a] Johnson obtained at 30 C (with 0.01 per cent consistency) $pv = 24875.08 + 11.802\,p - 0.001094\,p^2$ (cc atm/mole).

retical calculation of the second virial coefficient of this gas is the one by de Boer and Michels (35, 36). The results of these theoretical calculations are in excellent agreement with the experimental data. Keyes (80) gives the following formula for the second virial coefficient of helium

$$B = \tau^{1/4}\,(16.4873 - 74.09\,\tau^{1/2} - 24.6\,\tau)\ \text{(cc per g)}$$

with the same notation as in the formulas previously quoted for the second virial coefficients of hydrogen and nitrogen.

The vapor pressure of helium has also been investigated quite thoroughly (15, 16, 68, 74, 84, 138, 139). Bleaney, et al (15, 16) have measured the vapor pressure of liquid helium from about 0.8 deg K to 1.6 deg K. They have formulated their values in a manner consistent with the identical relations of thermodynamics. Keesom (69) lists different formulas for the vapor pressure of helium on various temperature ranges. The normal boiling point of helium is 4.216 deg K; at the λ-point, $T = 2.186$ deg K, $p = 3.83$ cm Hg (138, 139). The critical constants of helium are (69)

$$\begin{aligned} T_c &= 5.20 \text{ deg K} \\ p_c &= 2.26 \text{ atm} \\ d_c &= 0.06930 \text{ g per cc} \end{aligned}$$

(*h*) *Argon.* The most important p-v-T data for argon are summarized in Table 8.

TABLE 8 COMPRESSIBILITY DATA FOR ARGON

Reference	Temp range, deg C	Max press, atm
Leiden isotherms[a] (124)	—150 to 20	60
PTR isotherms (52, 59, 60, 63)	—100 to 400	200
Masson and Dolley (92)	25	125

[a] The Leiden data for argon are in error according to Cragoe (28).

The vapor pressure of liquid argon from 84 to 90 deg K is represented very accurately by the formula (38)

$$\log_{10} p_{mm} = -\frac{339.3}{T} + 1.75 \log_{10} T - 0.006737\,T + 3.9506$$

where p_{mm} is the vapor pressure in mm Hg. The normal boiling point of argon is 87.3 deg K (43). The triple point of argon is 83.9 deg K (56). The critical constants of argon are (64)

$$\begin{aligned} t_c &= -122.4 \text{ deg C} \\ p_c &= 48.0 \text{ atm} \\ d_c &= 0.531 \text{ g per cc} \end{aligned}$$

(*i*) *Mercury.* Practically no significant p-v-T data are available for mercury. The only recent determination is the one of Klemm and Kilian (86, 87) at 500 and 1000 C, and pressures lower than 1 atm. The accuracy of their measurements is insufficient to deduce any information on the equation of state for mercury. The very extensive literature on the vapor pressure of mercury has been reviewed by Ditchburn and Gilmour (38), who give the following equations (except for an obvious mistake in sign, which is corrected here):

$$\log_{10} p_{mm} = -\frac{3308}{T} - 0.8 \log_{10} T + 10.3735 \ \text{(for liquid Hg)}$$

$$\log_{10} p_{mm} = -\frac{3347}{T} + 8.641 \ \text{(for solid Hg)}$$

where p_{mm} is the vapor pressure in mm Hg. The normal boiling point of mercury according to Blaisdell and Kaye (14) is 356.57 C on the international scale, or 356.7 C on the thermodynamic scale. The melting curve of mercury has been determined by Michels, et al (105) to 3000 atm. The critical constants of mercury are (64)

$$\begin{aligned} t_c &= 1650 \text{ deg C} \\ p_c &= 3500 \text{ atm} \\ d_c &= 5 \text{ g per cc} \end{aligned}$$

(*j*) *Gaseous Mixtures.* A limited amount of p-v-T data for few binary mixtures is available, but practically no information is available on mixtures of three or more gases, with the exception of air, which has been discussed previously. Only in the case of H_2–N_2 mixtures may the available information be considered sufficiently complete. A summary of the most important available data on binary mixtures is given in Table 9. In addition to the references listed in Table 9, the following references may be mentioned: Edwards and Roseveare (41) have determined second virial coefficients of the following binary mixtures at 25 deg C: H_2-N_2, H_2-CO_2, N_2-CO_2, O_2-CO_2, H_2-C_2H_4, CO_2-C_2H_4, N_2-C_2H_4, He-N_2, He-CO_2. The method used by Edwards and Roseveare appears capable of great accuracy, but it requires the knowledge of the second virial coefficients of the pure gases. To date this method has been used only at low pressures and only at a single temperature. Gerry (44) has determined second virial coefficients for H_2O-CO_2 mixtures from 50 to 90 C. Bartlett (5) has obtained some data on the H_2O-N_2 system, but these data appear to be only moderately accurate. Markham and Kobe have carried out some measurements at 25 C and approximately atmospheric pressure with mixtures of O_2, N_2, CO_2, N_2O (91). The system N_2-H_2-NH_3 has been investigated by Kazarnovskii, et al (66).

TABLE 9 COMPRESSIBILITY DATA FOR GASEOUS MIXTURES

Reference	Mixture	Temp range, deg C	Max press, atm
Verschoyle (ref. 150)	H_2–N_2	0 and 20	205
Bartlett, et al (ref. 6, 7, 8)	H_2–N_2	—70 to 400	1000
Wiebe and Gaddy (ref. 152)	H_2–N_2	0 to 300	1000
Holborn and Otto (ref. 59)	Ne–He	0 to 400	100
Gibby, et al (ref. 46)	H_2–He	25 to 175	125
Haney and Bliss (ref. 48)	N_2–CO_2	25 to 125	500
Keyes and Burks (ref. 81)	N_2–CH_4	0 to 200	300
Masson and Dolley (ref. 92)	O_2–A	25	125
Torocheshnikov (ref. 146)	N_2–CO	—200 to —150	25
Scott (ref. 140)	H_2–CO	25	170
Townend and Bhatt (ref. 147)	H_2–CO	0 and 25	600

Conclusions

The temperature and pressure ranges covered by available p-v-T data for H_2, N_2, O_2, CO, CO_2, Air, He, A, Hg, and their mixtures have been summarized in the paper. Fig. 1 illustrates the substance of this summary. The available data are amply adequate in the case of helium and hydrogen; for these gases, measurements have been carried out over an extremely wide temperature range, and moreover the theory has been developed to such a point that the formulation of the existing data must be considered quite reliable. The data for argon, nitrogen, and air are not as extensive, but are probably sufficient for most practical purposes. The range covered by the data for oxygen, carbon monoxide, and carbon dioxide does not appear sufficient to allow reliable extrapolation to the high temperatures of interest in gas-turbine design or to the low temperatures of interest in liquefaction processes.

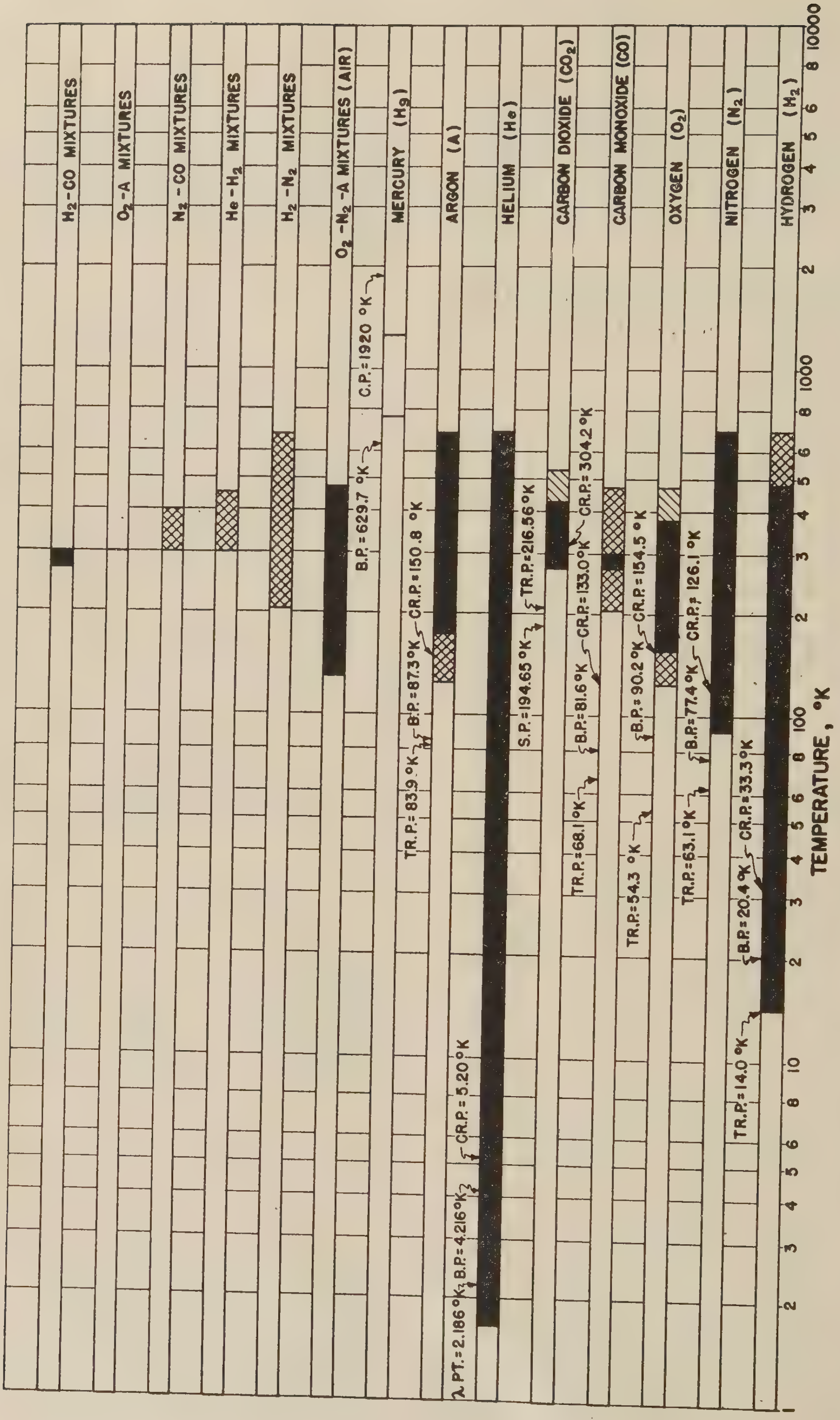

Fig. 1 Temperature Range Covered by Available Compressibility Data for Some Gases and Their Mixtures

No significant compressibility data are available for mercury. With the possible exception of the hydrogen-nitrogen system, the available p-v-T data for gaseous mixtures are definitely inadequate.

The vapor pressures of the substances considered in this report have been determined with sufficient accuracy in so far as the pure gases are concerned. However, with few exceptions, the data on liquid-vapor equilibrium for mixtures of these substances are definitely inadequate.

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V—Vapor Pressure, Specific Volumes, and p-v-T Data for H_2O, NH_3, CH_4, C_2H_4 With Comments on Mixtures

By F. G. Keyes,[1] Cambridge, Mass.

Because of its importance wherever thermodynamics is used, reference is made to the need of improved knowledge of the relation of the international scale of 1927 to the thermodynamic scale. The published results of James A. Beattie comprise comparisons between the scales from 32 F to 832.28 F and indicate that the thermodynamic-scale temperature as a maximum is 0.26 deg F greater than the international scale at about 750 F. The new thermometric information makes possible a thermodynamic consistency test of vaporization data, vapor pressures, and volume data from the steam investigation sponsored by this Society up to 1935. It is suggested that additional volume data are desirable above 860 F. Comments are offered on the known thermodynamic properties of water, ammonia, methane, ethylene, and mixtures of a number of the eleven pure gases of the list selected by the Research Committee on Properties of Gases and Gas Mixtures.

Introduction

The vapor pressures, specific volumes, and heat quantities for the substances water, ammonia, methane, and ethylene, and mixtures, are considered in the present paper. Under the steam-research program, sponsored by this Society, our knowledge of all thermodynamic properties of water and steam came to exceed that of any substance in the range of pressure and temperature experimentally determined. The accuracy and consistency of the data provided by the international co-operative effort fostered by the Steam Research Committee is an impressive example of the enduring value of a broadly conceived and executed program of research. It will be recalled that the stimulus which led to the formation of the old Technical Subcommittee of the Special Research Committee of the steam-research group, under the chairmanship of George A. Orrok, was the complete lack of data in the ranges of pressure and temperature desired for advanced steam-turbine design. A similar stimulus exists now prompting the verification of the existing data and the suggestion, where needed, of new experimental research over extended ranges of pressure and temperature in the interest of sound progress in the design of gas turbines, rocket motors of various types, and other problems of applied thermodynamics. In addition, attention to the nonthermodynamic data, viscosity, heat conduction, sound velocities, spectroscopic properties, absorption, and emissivity of radiation, is required for the solution of problems of design where heat transmission under flow conditions enter.

At the time of the first Steam Research Committee meeting (1921), the program proposed seemed formidable indeed, and the time estimated was to run several years to reach the proposed goal. To one who took part in the earlier program, the present proposed objective appears, if not more difficult, much more diversified, and perhaps years of effort may be required to satisfy the needs of the rapid developments in applied mechanical engineering. The practical need for the results is evidently increasingly insistent, and engineering design may ill afford the delays and frustrations which the lack of accurate basic data entails.

It is of interest at this time to note that under the Department of Scientific and Industrial Research of the British Government, a comprehensive mechanical-engineering program of research will be carried out. The broad list includes research on heat transfer, properties of substances, and mechanics of fluids. In the interest of conservation of effort and experimental resources, it might be desirable to promote international co-operation in the proposed broad program of research of the present ASME Special Research Committee, along lines resembling the steam-research program.

The Properties of Water and Steam

In the report on the Third International Steam Tables Conference (1)[2] of 1935, there will be found a reference to commitments made by several of the participating national groups with respect to further research. In fulfillment of the commitments, Osborne, Stimson, and Ginnings carried out a highly important series of vaporization measurements from 0 to 100 C. The heat capacity of liquid water in the same range was also measured. Abroad, in 1939, an investigation of volumes in the critical region of water was reported upon by Hans Eck (2), which substantially confirmed the values obtained earlier by Osborne, Stimson, and Ginnings, and by Smith and Keyes. The group (3) at the Massachusetts Institute of Technology reported in 1938, upon measurements of the change of enthalpy of the vapor with pressure at constant temperature in the region from about 40 to 125 C begun in 1932. The latter measurements supplied data of state in a region below 100 C by a flow method, thereby providing important information which had been unobtainable earlier by usual methods.

There also appeared independent precise information on vapor pressures in the region 73.5 to 128.6 C by Moser and Zmaczynski (4), in 1939, working at the Reichsanstalt. These data are of special value in view of the fact that no exact measurements of the vapor pressure of water have appeared in this region since the publication of a correlative summary of the early material in 1919, by Scheel and Heuse.

Publications reporting the results of an investigation of fundamental importance in all fields of applied thermodynamics began to appear in 1930. This research (nine published papers by James A. Beattie and his collaborators, D. D. Jacobus, J. Kaye, J. M. Gaines, Jr., T. C. Huang, M. Benedict, H. T. Gerry, C. A. Johnson, and B. E. Blaisdell, working at M.I.T.) established the temperature of melting ice on the thermodynamic scale to be

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[1] Professor of Physical Chemistry, Massachusetts Institute of Technology.

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-165.

[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

273.16 ± 0.01 deg K, or 459.69 ± 0.02 deg F; and developing high accuracy in the use of the gas thermometer, obtained a new value for the normal boiling point of sulphur, a fundamental calibration point for the present international scale (1927). The value obtained by Beattie and his colleagues indicated a value higher than the accepted sulphur point (444.6 C) by at least 0.1 deg C for the thermodynamic temperature. The normal boiling point of mercury (356.58 C) was also determined on the thermodynamic scale and found to differ from the temperature indicated by the platinum resistance thermometer under specifications of the international scale of 1927. Dr. Beattie has generously provided data for a graph, Fig.1, showing the differences his investigations provide for the departure of the international scale from the present international scale. Fig. 2 shows the parts per thousand differences in the vapor pressure of water due to the temperature differences appearing in Fig. 1.[3]

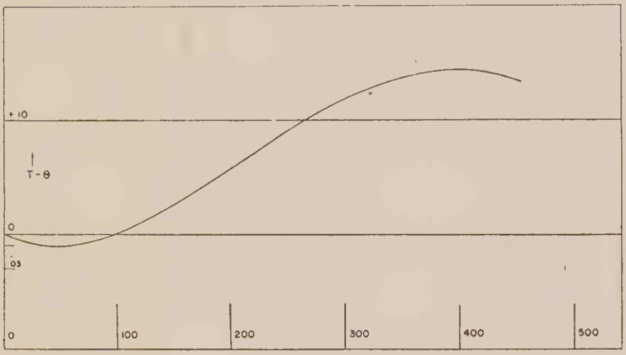

Fig. 1

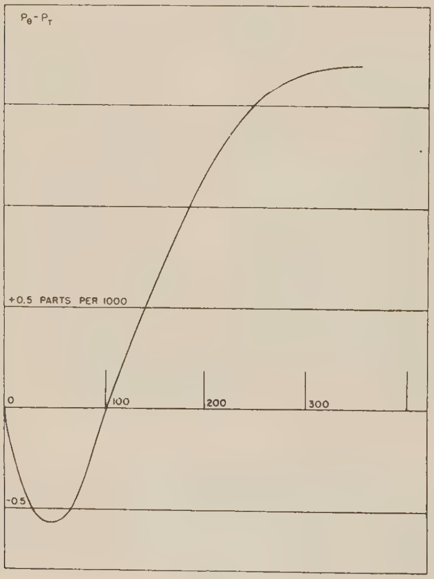

Fig. 2

The correlation of thermodynamic data, their testing for consistency and precision, can be relied upon only to the extent that our knowledge of the relation of temperature-indicating devices (secondary thermometers) to the thermodynamic scale can be perfected. Gas-thermometer readings suitably extrapolated to zero pressure are a primary standard and indeed are the most practical means of realizing the thermodynamic temperature.

At present, modern gas-thermometer practice, represented by Beattie's published contributions, extend from 0 to 444.7 C, whereas it is essential that the investigations be carried to the gold point (1063 C or 1945.4 F). The latter temperature is sufficient to establish certain connection with the radiation pyrometer for accurate measurements of higher temperatures.

The use of the new data on the relation of the international scale of temperatures to the thermodynamic scale is exemplified through the intercorrelation of the available water-vaporization measurements of Osborne, Stimson, and Ginnings, the vapor-pressure values of water from three independent sets of measurements by Egerton and Callendar, Osborne, Stimson, Fioch and Ginnings, and Keyes, Smith, and Gerry, all in excellent agreement and the values reported for the volume of steam obtained by Keyes, Smith, and Gerry, supplemented by the measurements of Collins and Keyes. All of these measurements were made using precision platinum resistance thermometry in accordance with the specifications of the international scale of 1927. Accordingly, in view of the high accuracy of the steam data, a correlation through the equations of thermodynamics of the vaporization data with the volume data should be satisfactory if use is made of Beattie's difference required to convert international temperature assignments to thermodynamic-scale values.

The process of making the calculations begins with a listing of the data (Bur. Stand. RP 983) for the vaporization quantity, γ, together with the temperature-scale difference, $T - \theta$, where T designates thermodynamic-scale temperature, and θ the corresponding international scale, and the values of $dp/d\theta$ and $v_{s\theta}\, \theta\, dp/d\theta$ are available. From the thermodynamic equation $\gamma = v_s\, T\, dp/dT$, where v_s is the specific volume of the saturated vapor, and p the pressure, the specific volume v_s may be computed provided $d\theta/dT$ is available. Finally, if the values of v_s and T are substituted in the equation of correlation for the volume data $p = f(v,T)$, the resulting pressures should agree with the directly measured values of pressure corrected of course to the thermodynamic scale from the international scale on which the measurements were taken. The result is given in Table 1 and a deviation graph in Fig. 3.[4]

Additional Steam Data Desirable. The most urgent need in the case of steam is for data in the range above 460 C or 860 F; the limit of the earlier steam investigation. Data above this temperature are not required to pressures higher than 80 atm or about 1176 psia. It is believed that in the desired temperature range the use of the flow method to measure the change of the enthalpy with pressure at constant temperature would provide the most exact data in the most convenient way. It would also be desirable to have new measurements on the vapor pressure of water from 0 to 150 C, using the highly precise and reproducible platinum re-

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[3] A summary of important results of the thermometric investigation will be found in "Temperature," published by Reinhold Publishing Corporation, in 1941, under the names of J. A. Beattie, B. E. Blaisdell, and Joseph Kaye.

[4] It will be recalled that the equation of correlation for pressure, volume, and temperature, or equation of state, is based upon the ideal gas laws $p = RT/v$, where T is the true thermodynamic temperature. Accordingly, when the deviations are small, or for (RT/pv) not greatly exceeding unity, the equation of state gives pressures approximately on the absolute scale even if the constants are not known with the highest accuracy. The equation of state used in the foregoing correlation is as follows

$$\log RT/p\omega = \psi\omega\rho^2$$

where

$$\omega = v - \delta,\ \delta = \beta \exp. (-\alpha\rho)$$

$$\psi = \psi_0 (1 + \psi_1\rho) \text{ where } \rho \text{ is density, and}$$

$$\psi_0 = \bar{A}_0 \tau \exp. c_2\tau^2, \text{ where } \tau = T^{-1}$$

$$\psi_1 = \bar{A}_1\psi_0^2 \exp. c_2\tau^2$$

$$\{\beta, \bar{A}_1, [\alpha, \bar{A}_0, c_2 \text{ (base 10)}] \text{ are constants}\}$$

$(\beta = 2.0624;\ \alpha = 0.38;\ c_2 = 7.4238 \cdot 10^4;\ \bar{A}_0 = 1260.17;\ \bar{A}_1 = 0.24253)$

Units are: cc per gram, normal atm. $T = 273.16 + t$ deg C.

TABLE 1 TEST OF THERMODYNAMIC CONSISTENCY FOR VAPORIZATION—VAPOR PRESSURE AND VOLUME DATA FOR STEAM[a]

t	v_s calc	p_{calc}	p_{obs}
0	206381.0	0.006025	0.006026
50	12038.6	0.121797	0.121786
100	1673.4	0.99987	1.00000
150	392.80	4.695	4.695
170	242.79	7.810	7.811
180	193.993	9.887	9.887
190	156.47	12.377	12.375
200	127.290	15.331	15.329
210	104.346	18.811	18.807
220	86.129	22.872	22.867
230	71.530	27.579	27.573
240	59.723	32.997	32.994
250	50.097	39.196	39.197
260	42.184	46.254	46.256
270	35.636	54.231	54.247
280	30.165	63.226	63.250
290	25.565	73.322	73.351
300	21.658	84.637	84.646
310	18.337	97.215	97.238
320	15.470	111.224	111.232
330	12.984	126.740	126.744
340	10.795	143.913	143.925
350	8.821	162.943	162.923
360	6.960	184.011	183.977

[a] v_s calc = from vaporization data and vapor-pressure data from formula $\gamma = v_s T\, dp/dT$, using J. A. Beattie's comparison of the thermodynamic and international temperature scale

p_{calc} = pressure given by equation of state based upon volume data for superheated steam

p_{obs} = vapor pressure observed on international temperature scale, but reduced to thermodynamic scale using Beattie's data

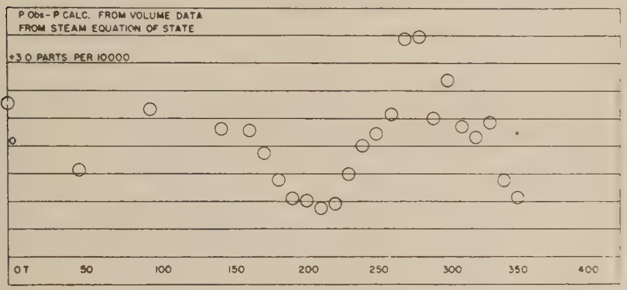

FIG. 3

sistance thermometer. Aside from the foregoing suggestions, the thermodynamic data for water are complete and highly exact.[5]

PROPERTIES OF AMMONIA, VAPOR AND LIQUID

The data for this substance are neither as complete nor as accurate as for water substance. Additional vaporization data are needed above 50 C or 90 F, and to the critical temperature, about 132.9 C or 238.4 F. The volume data extend from —35 C to 325 C, and the temperature range should be extended, but because of the instability of ammonia it would be difficult to exceed 500 C even with flow methods. However, for all present practical purposes, volume data at higher temperatures do not appear necessary.

Additional Ammonia Data Desirable. The specific volumes of the liquid phase above 50 C or 122 F should be verified as well as the volumes for compressed liquid from 0 to 132 C. The specific heat or enthalpy of the saturated liquid is also required above 50 C, and, in addition, vapor-pressure measurements above this temperature would be welcome.

PROPERTIES OF METHANE

Data for this substance in the region below the critical state (t_c = —82.5 C or —116.5 F) are fairly complete. The vapor-pressure and saturation-liquid specific volumes (5) above 1 atm pressure might be verified, and also the vapor pressure of the solid phase. Values for the pressure-volume properties are available (6, 7, 8) in the range 0 to 200 C to about 300 atm. There is great need of pressure-volume data below the critical temperature for the gas phase (p_c is 45.8 atm) and also for the liquid phase.

Additional Methane Data Desirable. Data on the vaporization quantities for the two-phase range virtually do not exist and are of great importance for all substances in view of the industrial and theoretical importance of perfecting our knowledge of liquid and gaseous mixtures. The specific heat of the liquid phase is known for 96 deg K only (9), and, accordingly, a comprehensive investigation is required.

The specific-heat data of the solid phase are fairly complete, but the vapor pressure of the solid phase requires verification.

Methane is one of the most abundant and potentially valuable natural assets the United States possesses, and full information on physical properties is important.

PROPERTIES OF ETHYLENE

Ethylene is chemically an unsaturated hydrocarbon. Its critical temperature is 9.7 C or 49.46 F, and critical pressure 50.9 atm.; melting point —169.4 C or —272.92 F. The substance has interesting possibilities as a refrigerant for very low temperatures. From the chemical point of view the substance is of fundamental importance.

The pressure-volume behavior of ethylene has been obtained by Amagat (10), and Masson and Dolley (11). More recently Michel and Geldermann (12) have published measurements of the volume beginning at 0 C and extending to 150 C, and to pressures of 3000 atm. Only a small portion of the vapor-pressure curve (13, 14, 15) has been measured over the long liquid range 179 C. The vaporization values are entirely absent and also the specific heat of the liquid phase.

Additional Ethylene Data Desirable. Volume measurements below 0 C extending to —50 C are needed for both the vapor and liquid phases. The vapor-pressure curve requires extension from —47 C to the critical temperature.

Complete heat-of-vaporization measurements are required, and the specific heat of the liquid phase.

QUESTION OF MIXTURES

The technically important mixture of the list of gases is air, comprised of nitrogen, oxygen, and argon as most abundant constitutents. In spite of its great importance, the ternary mixture has not been sufficiently investigated to satisfy completely the requirements of the oxygen industry.

The binary mixtures comprised of the pure gases of the list which have received some attention are methane-carbon dioxide (16) from 38 C to 238 C and 680 atm, for four mixtures and methane-water for the same range. Some data also exist for argon-oxygen, argon-nitrogen, argon-ethylene, oxygen-nitrogen, oxygen-carbon dioxide, oxygen-ethylene, hydrogen-carbon dioxide, hydrogen-nitrogen, nitrogen-methane. However, these data are in no case complete in the sense that a wide range of temperature or pressure has been covered, and the two-phase region is very incomplete. No vaporization measurements have been made, except in the case of nitrogen-oxygen (17). There are practically no heat-of-vaporization measurements except for the latter mixture (18). The specific heat of liquid mixtures is also entirely lacking.

Industrially, ammonia-water mixtures are of great importance in the refrigerating industry; and considerable, though incomplete, data exist. The author finds, however, that the disagreement in the results of different investigators is large, particularly for the compositions of the vapor phase in equilibrium with liquid mixtures.

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[5] The limitation of spectroscopic data for water and other substances required for a highly satisfactory calculation of Cp^0 for the vapors of the twelve gases, is discussed in Part II of this series by Dr. Herzberg.

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VI—Dielectric-Constant and Refractivity Data

By J. G. Miller,[1] Philadelphia, Pa.

The dielectric constant and refractivity data already established at lower pressures for the twelve gases under consideration need little improvement. A few outstanding gaps in these data are specified. Accurate high-pressure data have been published for only a few of the gases, principally hydrogen, nitrogen, carbon dioxide, and ammonia. Even with these four gases, improvement in the techniques of measuring dielectric constants at high pressures is needed so that more accurate and more extensive studies can be made.

Dielectric-constant data for gases are used principally to evaluate the molar dielectric polarization P, according to the Clausius-Mosotti function

$$P = \frac{\epsilon - 1}{\epsilon + 2} \; \frac{M}{d}$$

where ϵ is the dielectric constant of the gas at density d, and M is the molecular weight. The P values are of importance because of their relation to the polarizability, α, and permanent electric moment μ (commonly called the dipole moment), of the molecules of the gas. In turn, the polarizability and dipole moment are used in calculating the intermolecular potentials for the estimation of virial coefficients in p-v-T studies.

Low-Pressure Data

At low densities, corresponding to pressures in the neighborhood of 1 atm, and at the relatively low frequencies at which dielectric constants are most accurately measured, the Debye equation has been shown valid in the form

$$P = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

where N and k are Avogadro's number and Boltzmann's constant, respectively, with T the absolute temperature. This equation shows that if no transitions in intramolecular states occur with changing temperature, the dipole-moment value may be obtained from the slope of a plot of P against $1/T$, the intercept determining the polarizability. This temperature-variation method is regarded as the most accurate one for measuring dipole moments.

A second method of determining dipole moments utilizes the Lorentz-Lorenz[2] function for the molar refraction R, in terms of the square of the index of refraction n

$$R = \frac{n^2 - 1}{n^2 + 2} \; \frac{M}{d}$$

The n values are most accurately measured at frequencies in or near the visible spectrum. If these values are extrapolated to infinite wave length, and the n_∞ value so obtained is substituted in the L-L function, the molar refraction R_∞, that results is a constant for the gas. The R_∞ value measures the induced polarization, that is, the part of the dielectric polarization P, in excess of the contribution by the permanent dipoles

$$R_\infty = \frac{4\pi N}{3}\,\alpha$$

Thus if P and R_∞ are determined at the same single temperature, the value of μ can be calculated readily from the two figures. The values of α and μ are usually in good agreement with the estimates obtained by the first method in the case of diatomic molecules where infrared vibrations are absent or contribute little to the dielectric constant. Agreement for polyatomic molecules can be exact only in those rare cases where the extrapolations of the refraction data employ dispersion formulas which include the infrared-vibration terms. The contribution of infrared terms to the dielectric polarization is commonly called the "atomic polarization."

The dipole moments of all the gases under discussion have been determined satisfactorily by the temperature-variation method. Table 1 lists the most accurate values determined at low pressures in that way.

TABLE 1 DIPOLE-MOMENT VALUES DETERMINED BY TEMPERATURE-VARIATION METHOD AT LOW PRESSURES

Gas	$\mu \times 10^{18}$ e.s.u.	Bibliography reference (date)
Ammonia	1.48	1(1926)
	1.44	2(1927)
	1.47	3(1935)
	1.44	4(1946)
Argon	0	5(1927)
	0.03	6(1931)
Carbon dioxide	0.06	1(1926)
	0	7(1928)
	0	8(1934)
	0	9(1937)
	0	4(1946)
Carbon monoxide	0.10	10(1928)
	0.10	8(1934)
	0.11	11(1943)
Ethylene	0	12(1925)
	0	8(1934)
Helium	<0.015	6(1931)
	0	11(1943)
Hydrogen	0	5(1927)
	<0.015	6(1931)
	0	11(1943)
	0	4(1946)
Mercury	0	13(1936)
Methane	0	14(1919)
	0	15(1926)
	0	8(1934)
Nitrogen	0	1(1926)
	0	8(1934)
Oxygen	0	8(1934)
	0	11(1943)
Water vapor	1.84	16(1930)
	1.84	17(1935)
	1.83	18(1935)

It is noted that, except for NH_3, CO, and H_2O, these gases are nonpolar, the dipole moments being zero within the experimental error. Of these nonpolar molecules, only the case of CO_2 has caused contention during its history, the earlier, less accurate,

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[2] Hereafter in this paper the Clausius-Mosotti and Lorentz-Lorenz functions will be referred to by the symbols C-M and L-L.

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temperature-variation measurements indicating a μ value of approximately 0.1×10^{-18} e.s.u. for this molecule.

It is unsafe to judge the status of the low-pressure dielectric-constant data for these gases only by the agreement shown for the dipole moments determined in this way. The excellence of the results may depend more on the precision of the measurements than upon their absolute accuracy because the temperature coefficient of the dielectric constant rather than the constant itself determines the accuracy of the dipole moment obtained.

The absolute accuracy of the data is better tested by the second method, especially in the case of the nonpolar gases. According to this method, P should equal R_∞, which requires that ϵ and n^2_∞ should be equal at the same density and temperature for such gases. The comparison is conveniently made with the N.T.P. values of these quantities because the data are usually reduced to these figures in the literature. The test is in most cases a safe one because refractivity data are usually highly accurate.

Table 2 presents the most accurate N.T.P. data obtained from dielectric-constant measurements made at low pressures for the nonpolar gases. In each case, the data obtained from the dipole-moment studies, reported in Table 1, have been listed. In addition, in most cases there are shown data from measurements made primarily to establish the absolute values of the dielectric constants. Dielectric-constant values, determined before 1920, are not reliable because modern techniques were not available before that date. For historical interest, some of the earlier values are listed, together with some International Critical Tables figures.

TABLE 2 N.T.P. VALUES OF DIELECTRIC CONSTANTS OBTAINED FROM LOW-PRESSURE DATA AND N.T.P. EXTRAPOLATED REFRACTIVE INDICES OF NONPOLAR GASES

	ϵ	Bibliography reference (date)	n^2_∞	Bibliography reference (date)
Argon	1.000550[a]	5 (1927)	1.000556[b]	22 (1924)
	1.00056	19 (1929)	1.000555[d]	23 (1932)
	1.000553[a]	20 (1929)	1.000554[b]	24 (1940)
	1.000550	6 (1931)		
	1.000545	21 (1946)		
Carbon dioxide	1.000980[c]	1 (1926)	1.000882[b]	25 (1920)
	1.000987	7 (1928)	1.000975[d]	26 (1928)
	1.00098	19 (1929)	1.000884[b]	24 (1940)
	1.000989[c]	8 (1934)		
	1.000982[c]	9 (1937)		
	1.000986[c]	59 (1944)		
	1.000997[c]	4 (1946)		
Ethylene	1.00146	27 (1885)	1.00137[b]	28 (1931)
	1.00145[c]	12 (1925)		
	1.00145[c]	8 (1934)		
Helium	1.000074	29 (1908)	1.000068[b]	30 (1908)
	1.000073	6 (1931)	1.000069	31 (1925)
	1.000070[c]	11 (1943)	1.000070	6 (1931)
	1.000068	21 (1946)	1.000069[b]	23 (1932)
Hydrogen	1.000265	32 (1924)	1.000272	33 (1909)
	1.000259	5 (1927)	1.000272[b]	34 (1921)
	1.000275	6 (1931)		
	1.000264[c]	11 (1943)		
	1.000268[c]	4 (1946)		
	1.000272	21 (1946)		
Mercury	1.00182	35 (1922)	1.00170[b]	36 (1933)
	1.00170	13 (1936)		
Methane	1.00094	37 (1874)	1.000884[d]	38 (1940)
	1.00095	27 (1885)		
	1.00094[c]	14 (1919)		
	1.00096	15 (1926)		
	1.000878[c]	8 (1934)		
	1.000878[c]	9 (1937)		
Nitrogen	1.000581	1 (1926)	1.000589[b]	41 (1910)
	1.000589	39 (1931)	1.000586	42 (1934)
	1.000587[c]	8 (1934)	1.000588[b]	43 (1936)
	1.000579	40 (1939)		
	1.000580	21 (1946)		
Oxygen	1.000547	44 (1910)	1.000528	33 (1909)
	1.000518	32 (1924)	1.000530[b]	45 (1927)
	1.00051	19 (1929)	1.000532[b]	46 (1932)
	1.000531[c]	8 (1934)	1.000531[b]	43 (1936)
	1.000542[c]	11 (1943)		
	1.000523	21 (1946)		

[a] Corrected by Hector and Woernley, Bibliography reference (21).

[b] Calculated by writer from refraction or dispersion data given in reference listed.

[c] Reduced to N.T.P. by writer.

[d] Dispersion formula used for extrapolation includes infrared vibration terms.

For argon, helium, hydrogen, nitrogen, and oxygen, it is apparent that the best measured values of $\epsilon - 1$ are equal to $n^2_\infty - 1$ within 1 to 2 per cent at low pressures. The refractivity data for these gases are at present more accurate than the dielectric-constant data. In view of this and the theoretical and experimental evidence shown for the equality between ϵ and n^2_∞ for these substances, it is suggested that this equality be accepted for them. In this way the important use of these gases as the most common and most reliable standards for gaseous dielectric-constant determinations would be improved, and further improvement would most readily be worked by increase in the accuracy of the refractivity and compressibility data.

The studies of mercury vapor by Wüsthoff and by Wolfsohn are the most accurate published to date. No improvement of their excellent results appears urgent in view of the lack of interest of the dielectric behavior of this gas.

No reliable dispersion formula including infrared terms has been published for ethylene. It is fairly certain that here the atomic polarization is considerable so that it is not surprising that the value of n^2_∞, obtained by the Lowery (28)[3] equation is lower than ϵ. The dielectric-constant values are self-consistent, and at present infrared-refraction data for this gas would be of importance both to test the dielectric-constant data and to aid our understanding of atomic polarization.[4]

In the case of methane, the earlier dielectric-constant values are definitely in question, owing to the careful refractivity studies of Rollefson and Havens and the dielectric-constant studies of Watson's group. Further experimentation dealing with the absolute value of ϵ for this gas is desirable.

The ϵ values for carbon dioxide are generally considered (47, 48) in satisfactory agreement with the value of n^2_∞ obtained from the Fuchs (26) dispersion formula, which includes the contribution of atomic polarization to the refractivity. Although the differences are small, in general, the consistency with which the ϵ values exceed the n^2_∞ value is of interest. The importance of this gas warrants further study of its refractivity. Despite the indirect evidence both for and against the anomalous rise in the dielectric constant in the temperature range 25 to 40 C, reported by Fox and Ryan (40), 1939, it is surprising that no further detailed investigation has been made to settle the question of its existence.

The data for the polar gases are not shown in Table 2. In the case of water and ammonia, the large moments make the contribution of α to ϵ much smaller than that of $\mu^2/(3kT)$, so that the test employing refraction data is quite uncertain (47). With carbon monoxide, where the moment is much smaller, no adequate dispersion formula is available for the test. It is apparent that the existing data for these three gases are satisfactory, except for the purpose of exact estimation of the atomic polarization.

Although water vapor (49) has been studied up to 150 megacycles without apparent change in its dielectric constant, the field of very high frequencies has not been investigated for the polar gases. Such studies are of interest in relation to anomalous dispersion studies in condensed media.

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[3] Reference numbers in Tables 1 and 2, and numbers in parentheses appearing in the remainder of the paper refer to the Bibliography at the end of the paper.

[4] Dr. E. Bright Wilson, Jr., has kindly called our attention to the work of A. M. Thorndike, A. J. Wells, and E. Bright Wilson, Jr. (*Journal of Chemical Physics*, vol. 15, 1947, pp. 157–165) in which, from a study of the absorption intensities of the chief infrared absorption bands of ethylene, they have estimated the atomic polarization of that substance in good agreement with the values determined from the visible index and the dielectric constant by Watson and Ramaswamy (43). They also report that their values for the absorption intensities reproduce an observed dispersion curve constructed from unpublished data supplied them by R. Rollefson and R. Havens for the refractive index of ethylene.

Finally, for all of these gases, higher-temperature dielectric-constant data are lacking, although Goldschmidt and Hölemann (50) have studied the L-L function of carbon dioxide up to 800 C, noting a slight rise in the function above 400 C. They attribute this rise to excitation of higher vibration states. Further work would be useful in estimating the effect of higher vibration states on the polarizabilities and dipole moments of the gases.

In summarizing, we may cite the need of the following data at low pressures for the gases under discussion:

1 Infrared refractivity data to estimate the n^2_∞ values for ethylene, carbon dioxide, and carbon monoxide.

2 Dielectric-constant values for methane and carbon dioxide (between 25 and 50 C for CO_2).

3 High-frequency and high-temperature dielectric-constant data for all the stable gases.

High-Pressure Data

Data have been reported for several of these gases at high pressures. With increase in density, the magnitude of the dielectric constant rises so that increased accuracy can be gained in the determinations of ϵ, especially if pains are taken in designing the measuring condenser to prevent distortion under pressure. In this way, with accurate compressibility data available, the C-M function can be evaluated and extrapolated accurately to normal pressure. This has been done for several of the gases and, when combined with studies at several temperatures, has afforded valuable information concerning their dipole moments.

The most important use of the high-pressure values is, however, to guide theoretical work on the dielectric behavior of condensed systems. Gases serve well in this respect because their densities can be regulated to provide a continuous approach to the liquid-state conditions.

Such data are lacking or far from complete for argon, carbon monoxide, ethylene, helium, mercury, methane, oxygen, and water vapor. For argon, only the L-L function has been studied, Bennett (24) having shown that this function is constant at 0 and 30 C up to a pressure of 18.5 atm. The only C-M values mentioned in the literature for helium are some unpublished values obtained in Keyes' laboratory and stated (48) to show no trend with temperature or density. Methane has been studied only by Uhlig, Kirkwood, and Keyes (51). These workers showed that at 0 and 100 C and up to 175 atm, the C-M value is independent both of temperature and density. Oxygen was studied many years ago by Occhialini (52) at one temperature, 13.5 C, up to a density of 110 amagat, the C-M function being constant up to this density. Eadie and Satterly (53) studied the refraction behavior at 21 C, at 5210 Å, up to approximately 40 atm. Inspection of their data shows that the L-L function is constant over this range.

The high-pressure studies of hydrogen and nitrogen have been reviewed by Keyes and Oncley (48). Since no more work has been published for these substances since that time, we may conveniently draw from the conclusions presented in that review.

Extensive data by many workers on the C-M function of hydrogen show no systematic deviation for it with change in density and temperature between 0 and 100 C and pressures up to 1425 atm.

The dielectric behavior of nitrogen has been studied as extensively as that of hydrogen, temperatures from 0 to 150 C being used, and pressures up to 1000 atm. Keyes and Oncley summarize the data for nitrogen by stating that the C-M function by a faint apparent trend suggests the expectation of a positive density dependence. Theoretical study by Keyes' group (54, 55, 48) predicts that for hydrogen, helium, oxygen, and nitrogen, rise in pressure will indeed cause an increase in the C-M values. Unfortunately, the increase is close to the experimental error, which is about 1 in 500 over the range studied, the largest effect predicted being that for nitrogen, about 1 per cent at 1000 atm.

For both hydrogen and nitrogen, the high-pressure ϵ values, when extrapolated to N.T.P., agree very well with the values measured at low pressures and quoted in Table 2.

Keyes and Oncley cite the lack of L-L function data at high densities for structurally simple substances. The only data known are those of Magri (56) for air up to 200 atm at 15 C, of Eadie and Satterly for oxygen, and of Bennett for argon and for nitrogen (24) up to 13 atm at 0, 30, and 50 C. Over the limited pressure ranges pursued, the L-L function is constant for these gases.

The results of the dielectric-constant studies of carbon dioxide at high pressures have been the most perplexing. Following the early studies of Occhialini (52), which were carried up to only 50 amagat, the investigations were reopened by Keyes and Kirkwood (57) in 1930. In this and subsequent work at Keyes' laboratory, a rise in the C-M function was detected with initial rise in pressure. Later work in Michels' laboratory disagreed with this finding and, only after careful inspection of the experimental errors and correction of all the dielectric-polarization data available at the time, were Keyes and Oncley (48) able to bring the values into substantial agreement. Their study of the data revealed that the C-M function values showed an initial positive dependence on density but went through a maximum around 300 amagat and then decreased with rise in density. This conclusion was verified later by the extensive work of Michels and Kleerekoper (58) who carried their measurements to 1544 atm at 100 C, and 1687 atm at 50 C. Theoretical considerations (48, 55, 60, 61, 62) also confirm this behavior although the theory is incapable of predicting the position of the maximum at present. An additional achievement of the high-pressure measurements has been their strong confirmation of the nonpolarity of carbon dioxide.

The L-L function of carbon dioxide has received more attention at high pressures than that of any other gas. Phillips (63), Oleson and Bennett (64), and Michels and Hamers (65) have contributed the most accurate data, the last-named workers making their measurements at 25, 32, 50, and 100 C over a pressure range up to 2400 atm. The results of all these workers agree in showing a decrease in the L-L function with increases in pressure, no initial rise being noticeable. Furthermore, the decrease in the L-L function is not parallel with that of the C-M function. Lack of explanation of the difference in behavior of the C-M and L-L functions with increase in density mars the whole picture of the high-pressure studies.

Ammonia is the only polar gas whose dielectric behavior has been studied over a wide pressure range. It has been investigated only in Keyes' laboratory, but by several workers there. The results have been summarized by Keyes and Oncley (48). The measurements have yielded the important finding that the dipole moment of ammonia is independent of temperature and of density up to 4.48 moles per liter. Furthermore, the C-M function shows a definite positive trend with pressure, rising initially at the rate of 5 per cent per hundred atmospheres. The theoretical treatment of this C-M behavior is a difficult task, although some progress has been made on it (57, 54, 48, 66, 67).

Due to the small size of the effects produced in the values of the C-M and L-L functions by change in density, several of these gases, especially the simpler ones, should be studied over wider ranges of pressure and temperature than attempted to date. This will call for improved techniques, especially for the dielectric-constant measurements. At the same time, better p-v-T data will be required. Success with the simpler gases would prepare for similar extensive studies of carbon monoxide and ammonia.

High-frequency dielectric-constant measurements would be of even greater interest at high densities than at the lower pressures for the polar gases.

[Three publications dealing with pertinent material have appeared since this article was written. The first two, from Michels' Laboratory (A. Michels, H. Lebesque, L. Lebesque, and S. R. deGroot, *Physica*, vol. 13, 1947, pp. 337–342, and A. Michels, A. Botzen, and S. R. deGroot, *Physica*, vol. 13, 1947, pp. 343–348) report that the L-L functions of nitrogen, measured from 1 to 2000 atmospheres at 25 C, and of ethylene, from 1 to 2300 atmospheres at 25 and 100 C, show an initial increase with rise in pressure, pass through a maximum, and then decrease. While the maximum is pronounced only in the case of ethylene at 100 C, the final decrease is definite for both gases, in agreement with theory and the behavior shown by carbon dioxide.

The third publication, by A. van Itterbeck and K. deClippeleir (*Physica*, vol. 13, 1947, pp. 459–464) deals with the dielectric constant and the C-M function of carbon dioxide in the range 0 to 100 C and up to 16 atmospheres. The results agree well with the extrapolations of the higher pressure values of Michels and Kleerekoper (58) and show a maximum polarization in the neighborhood of 50 C. This work may well reopen the controversy concerning the structure of carbon dioxide (9, 40).]

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VII—A Summary of Experimental Determinations of Joule-Thomson Effects in Gases

By H. L. JOHNSTON[1] and DAVID WHITE[2]

A record is given of work on temperature effects which accompany the free expansion of gases from the classic experiments of Joule and Thomson in 1852–1862, down to present time. For purposes of summarizing present knowledge of Joule-Thomson data, more detailed information, which has been published since 1920, is included. Reliable methods are now available for the derivation of data of this character, which are of practical value in the thermodynamic treatment of gases under pressure. These are described briefly.

Introduction

THE classic experiments of Joule and Thomson (1, 2)[3] on the temperature effects that accompany the free expansion of gases, were performed between the years 1852 and 1862. Numerous investigators (3 to 21, inclusive) continued experiments of this type in the decades prior to 1920. Summaries of their work prior to 1905 and prior to 1919 are given by Kester (11) and by Hoxton (23), respectively. The objects of these investigations were: (*a*) the determination of gas liquefaction efficiencies; (*b*) measurements of enthalpy as a function of pressure; (*c*) measurements of heat capacity as a function of pressure; (*d*), evaluation of molecular attractive forces; (*e*) establishment of the ice-point temperature on the Kelvin Scale; and (*f*) checks on the reliability of high-pressure gaseous data of state. The work prior to 1920 may be summarized by the general statement that, with few exceptions (15, 16, 19, 20, 23), the data were limited in scope both with respect to pressure range and temperature range, and were generally lacking in experimental precision. The gases, represented in the few relatively good pieces of work prior to 1920, have since been examined with greater thoroughness and greater accuracy. For the purpose of summarizing present knowledge of Joule-Thomson data, reference therefore can be limited to work published since 1920.

Apparatus

Four types of apparatus have been used in measuring the Joule-Thomson effect: (*a*) throttling; (*b*) porous plug with axial flow; (*c*) porous plug with radial flow; and (*d*) the "isothermal method."

Joule and Thomson performed their initial experiments by the throttling method, which consists of measuring the temperature change which accompanies direct expansion through a needle valve or other orifice. They were unable to obtain reproducible results in their throttling experiments and quickly abandoned the method in favor of the porous plug.

The difficulties with the simple throttling method were clarified by the experimental work of Bradley and Hale (15), and that of Dalton (16). They arise from heat flow along the valve, exaggerated by the influence of the so-called "kinetic-jet" effect associated with the high-velocity gas stream, and from errors of temperature measurement on the downstream side of the valve, likewise due to the high gas velocity. Because of these difficulties the method was generally abandoned after 1909, although Dalton himself obtained good results, on air over rather limited pressure and temperature ranges, by use of a glass valve.

Recently, Johnston and co-workers (54, 55, 56) have overcome these difficulties with a valve of new design and have obtained good results on hydrogen and on deuterium down to 64 deg K.

The porous plug used by Joule and Thomson, and by most later workers, owes its advantage to the low thermal conductivity of the ceramic material from which it is usually fabricated. The original form of the plug used by Joule and Thomson, and by most subsequent workers up to 1920, was that of a solid cylinder. The gas flow through capillary pores in the material was parallel to the axis of the cylinder. This form of porous plug is today referred to as "porous plug with axial flow." Disadvantages were the necessarily large pressure drop required to force gas through the plug, and the relatively small rate of flow. There is also flow of heat in the metal housing around the plug.

The porous plug with axial flow is a distinct improvement over the earlier form of plug and is the form of porous plug generally used since 1920. The principle of the axial-flow plug was actually conceived by Regnault (3), shortly after Joule and Thomson's early work. Regnault passed the gas inward through the porous wall of a hollow enclosure. An opening through the wall carried off the low-pressure gas. Regnault himself abandoned Joule-Thomson experiments almost immediately, and his radial-flow plug escaped notice. It was developed, in improved form, into an apparatus of high accuracy by Burnett and Roebuck (18) in 1910, but experimental results on gases were not published by the latter authors until after 1920. Burnett and Roebuck's plug is a porous ceramic thimble of relatively thin wall. The gas passes inward through the wall of the thimble and flows out through the open end. This form of plug possesses advantages over the axial-flow plug both in the matter of heat leak and of increased flow of gas.

The isothermal method is essentially the throttling method with heat added to the cold low-pressure stream in sufficient amount to offset the Joule-Thomson cooling. The heat is supplied electrically, and from measurements of the heat added, the amount of gas passed through the valve, and a knowledge of the heat capacity of the low-pressure gas, the Joule-Thomson temperature drop can be computed. The method was first employed by Buckingham (13) in 1910, but was developed as an instrument for precision work by Keyes and Collins (41), and independently by Eucken, Clusius, and Berger (40) in 1932. This method reduces substantially the heat leak present in the original design of throttling apparatus, but does not remove it entirely because of the "kinetic-jet" effect. This effect is less prominent at low

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rates of mass flow, and so the isothermal method is best adapted to work at low pressures.

EXPERIMENTAL WORK

The most extensive program of Joule-Thomson effect measurements on inorganic gases, and probably the most accurate, has been that carried on at the University of Wisconsin by Roebuck and co-workers. Pure gases investigated have included air (27), N_2 (34), CO_2 (26, 36), He (32), and A (33). The pressure range was from 1 to 200 atm on all of the gases, and the temperature range was from 300 C down to —56 C for CO_2; to —100 C for air; to —150 C for N_2 and A, and to —190 C for He.

The Wisconsin data were taken with the radial-plug apparatus, and Joule-Thomson coefficients computed from the slopes of the isenthalps.

Roebuck and Osterburg (35, 37) also measured Joule-Thomson effects on helium and nitrogen, and helium and argon mixtures. Their earlier work (32) contained some data on mixtures of helium and air. The results with mixtures were rather surprising in that considerable amounts of the heavier impurity could be added to helium without much influence on the Joule-Thomson coefficients, but the coefficients for the heavier gases prove very sensitive to small amounts of helium. A proper theory for gas mixtures is practically nonexistent.

Knoblauch (28) and Haisen (29) have also measured Joule-Thomson effects in air, using an apparatus of the axial-flow type, in which the plug was made of asbestos. However, their data are more limited and less accurate than those obtained by Roebuck.

Eucken, Clusius, and Berger (40) used an isothermal throttling apparatus to measure Joule-Thomson effects in air at temperatures close to 200 C, and for pressures up to 50 atm.

Zelmanov (53), by means of throttling experiments, has determined the Joule-Thomson effect for helium for the temperature range 6 to 20 deg K and for pressures up to 60 atm. This supplements the data of Roebuck and Osterburg (32), but leaves a 60-deg gap.

Eumorfopoulos and Rai (30) also measured the Joule-Thomson effect in air by means of a radial-flow apparatus, up to pressures of 10 atm, and between 20 and 100 C, and obtained values a little higher than those found by Roebuck.

Keyes and Collins (41) have also furnished some data on both CO_2 and N_2, as well as on NH_3 and on water vapor. Their data were taken with the isothermal-expansion type of apparatus and were all under pressures of 5 atm. Some of the data for water vapor were for pressures as low as 50 mm. Except for some of the work with steam, which was carried to 125 C, temperatures were between 30 and 75 C. Their results were characterized by high accuracy (0.5 per cent in the measured heat), and their method is particularly adaptable to measurements at low pressures.

The data by Johnston and co-workers (54, 55, 56), obtained by an improved throttling apparatus, are the only reliable data on hydrogen, and on deuterium. The accuracy obtained in the measurement of Joule-Thomson effects is thought to be of the order of 1 per cent for deuterium, but may be a little less accurate than this for hydrogen, which was run before some improvements were made in the apparatus. The pressure range covered was from 17 to 200 atm. The temperature range was from 64 to 80 deg K, which is a region of interest in the operation of hydrogen liquefiers, and at 25 C.

Joule-Thomson data for steam were included in the systematic sets of determinations which preceded the preparation of the Steam Tables, by a committee of this Society. The accurate work of Keyes and Collins, who measured Joule-Thomson effects for steam up to 125 C, has already been referred to. The principal portion of the Joule-Thomson data for steam was collected by Kleinschmidt (25), who used a porous plug of alundum and who carried his measurements to 600 C. The pressure range was to 40 atm. Other data were supplied by Callendar (31), who used a type of calorimeter based upon the throttling principle.

This effectively summarizes the existing Joule-Thomson data on inorganic gases, including the very sparse material on their mixtures. A roughly equivalent amount of work has been done on hydrocarbon gases. Two groups of workers have participated in this program. One group, at the University of Michigan, under the direction of G. G. Brown, has used a throttling apparatus, similar to that used by Callendar (31) and embedded in a block of magnesia. They have determined data for naphtha and for pentane (39); for Dowtherm A (43), which is a mixture of diphenyl and diphenyl oxide; and for benzene (42). Pressures went to 70 atm for benzene, pentane, and naphtha, and to 30 atm for Dowtherm A. Temperatures were to about 100 C for naphtha and pentane; to 380 C for benzene; and to 500 C for Dowtherm.

The other group, at the California Institute of Technology, headed by Sage and Lacey, has employed apparatus with the radial-flow porous plug. An alundum fine-grained extraction thimble was used for the purpose. This group has obtained data (44 to 51, inclusive) on propane, normal butane, normal pentane, methane, ethane; and on mixtures of methane and ethane, of methane and butane, and of methane and propane. Their data were taken over the temperature range of 20 to 104 C, except for the last two mixtures for which data were taken to 150 C. Pressures went to 37 atm for propane; 15 atm for n-butane; 6 atm for n-pentane; 100 atm for methane; 40 atm for ethane, and to 100 atm for the three mixtures with methane. Sage and co-workers claim limits of accuracy that range from 1 to 3 per cent.

CONCLUSION

As this summary shows, there are no data at all for O_2, CO, NO, and C_2H_4, which are among the industrially important gases, and data are scant for NH_3, and H_2. There are no data for CH_4 below room temperature, and data for air, N_2, and A, which are among the more complete, extend down only to within 50 to 100 deg of their boiling points. There is a 60-deg gap in an important part of the temperature region for helium. Data on gas mixtures are limited to five examples.

Reliable methods are now developed for getting data of this character, which are of practical value in the thermodynamic treatment of gases under pressure. Whether or not data of this character are accumulated, in any quantity, will depend upon the interest of groups which are concerned with the development or operation of high-pressure processes, or which are interested in supporting basic scientific and engineering programs.

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VIII—Brief Review of Available Data on the Dynamic Viscosity and Thermal Conductivity for Twelve Gases

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A brief review of the available data relative to the dynamic viscosity and thermal conductivity for twelve gases is presented in order to show the need for future experimental work. The values found in the survey for the thermal conductivity and viscosity for the various gases at a pressure of approximately 1 atm have been analyzed and average values presented in the form of graphs to show the influence of the temperature.

INTRODUCTION

A REVIEW of the literature available to the author relative to the dynamic viscosity and thermal-conductivity values for ammonia (NH_3), argon (A), carbon dioxide (CO_2), carbon monoxide (CO), ethylene (C_2H_4), methane (CH_4), helium (He), hydrogen (H_2), mercury (Hg), nitrogen (N_2), oxygen (O_2), and steam (H_2O) has been made. The purpose of the review of the literature was to show the extent of the existing data, and to emphasize the need for future experimental investigations. It is realized that in the review of extensive literature it is often possible to overlook important sources of information. As a result, the author would appreciate receiving comments relative to any important work which has been overlooked.

AVAILABLE INFORMATION ON EACH GAS

The information found relating to the dynamic viscosity and thermal conductivity is discussed for each of the twelve gases.

Ammonia. All of the available data found in the literature dealing with the dynamic viscosity of ammonia are for a pressure of approximately 1 atm, and for temperatures ranging from —78.5 C to 441.1 C. The results reported in the various investigations were plotted and found to be in good agreement. Average values based upon the available data are well represented by a straight line as shown in Fig. 1.

Few data are available relative to the thermal conductivity of ammonia. The results which have been presented are based upon a pressure of 1 atm, cover a temperature range from approximately —60 C to 100 C, and are in fair agreement. Average values for the thermal conductivity as based upon the existing data for a pressure of 1 atm are plotted in Fig. 2.

Argon. All of the reported data dealing with the dynamic viscosity of argon are based upon a pressure of approximately 1 atm. The temperature range for this pressure is quite large, being —183 C to 1600 C. The various experimental results were plotted and were found to be in good agreement. The line shown in Fig. 1 represents average values for the complete range of temperature at a pressure of 1 atm.

The thermal conductivity of argon has been determined for a pressure of approximately 1 atm and for a temperature range from —183 C to 100 C. The experimental data are in good agreement, average values for which are plotted in Fig. 2.

Carbon Dioxide. All of the reported work except for one investigation deals specifically with the viscosity of carbon dioxide at a pressure of approximately 1 atm for a temperature range of —100 C to 1400 C. The agreement between the various data is satisfactory. Average values are represented by the curve in Fig. 1.

Phillips (50)[2] conducted experiments at five temperatures (20 C, 30 C, 32 C, 35 C, and 40 C) for pressures from 1 atm to 120 atm. These appear to be the only data showing the effect of pressure on the dynamic viscosity of carbon dioxide.

Numerous values for the thermal conductivity of carbon dioxide are available for a pressure of 1 atm, and a temperature range from —85 C to 600 C. Disagreement exists between the results of various investigators between 100 C and 600 C. A curve representing average values is shown in Fig. 2.

One investigation (109) covers a pressure range from 1 atm to 87 atm for temperatures ranging between 12 C to 50 C. At a temperature of approximately 37 C, the increase in conductivity for a pressure change from 1 atm to 87 atm was found to be over fivefold.

Carbon Monoxide. The viscosity data for carbon monoxide reported in the literature refer to a pressure of 1 atm and for temperatures varying from —192 C to 277 C. The curve shown in Fig. 1 represents the average values based upon all of the available data. The agreement between the data presented by the various investigators is quite satisfactory.

Values are available for the thermal conductivity of carbon monoxide at a pressure of approximately 1 atm and a temperature range from —190 C to 10 C. The existing data are in good agreement, average values of which are shown by the curve in Fig. 2.

Ethylene. The available reported viscosity data are based upon a pressure of approximately 1 atm and cover the temperature range from —79 C to 300 C. The agreement between the data of the various investigators is good, and no serious differences exist. The curve in Fig. 1 represents average values for a pressure of one atmosphere.

Several experimental investigations dealing with the thermal conductivity of ethylene have been made at atmospheric pressure and for a temperature range from —70 C to 100 C. The available data agree in a satisfactory manner, and a curve representing average values is shown in Fig. 2.

Methane. All of the viscosity data are based upon a pressure of 1 atm and cover a temperature range from —182 C to 499 C and are in good agreement. Average values based on the reported data are plotted in Fig. 1.

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NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-168.

[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

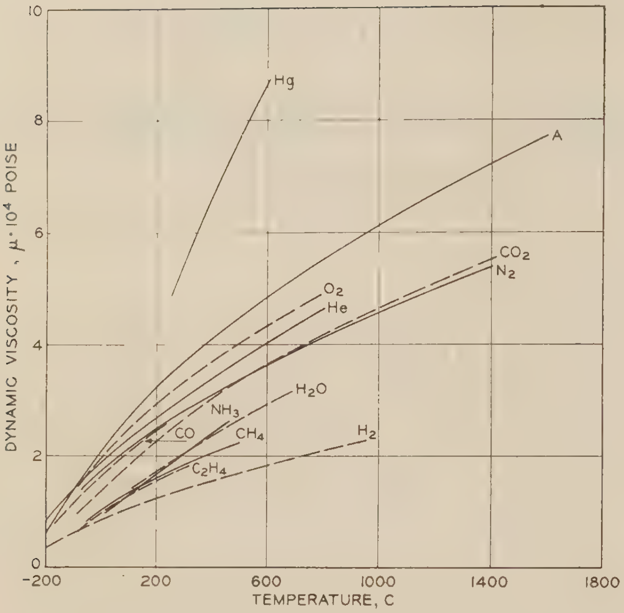

Fig. 1 Approximate Dynamic Viscosity Values for Several Gases at a Pressure of 1 Atm

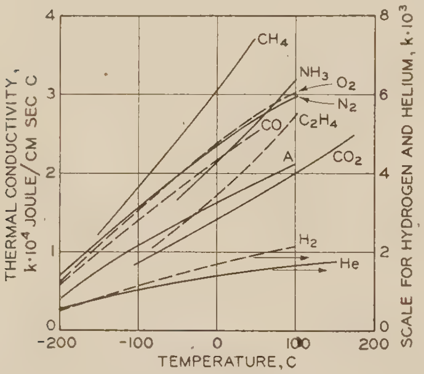

Fig. 2 Approximate Thermal Conductivity Values for Several Gases at a Pressure of 1 Atm

Values for the thermal conductivity of methane are available for a pressure of 1 atm and temperatures ranging from —180 C to 50 C. Serious disagreement exists at a temperature of 0 C. The available data have been plotted and the average values are shown in Fig. 2.

Helium. Except for some experimental viscosity data at a pressure of approximately $^1/_2$ atm, all of the other reported data are for a pressure of 1 atm and temperatures ranging from —260 C to 820 C. The data, in general, agree in a satisfactory manner. The curve in Fig. 1 represents average values for the available data.

Data are available for the thermal conductivity of helium for a pressure of 1 atm and temperatures ranging from —250 C to 100 C. The experimental values when plotted exhibit considerable scattering at temperatures below —100 C. Average values when plotted are represented by the curve in Fig. 2.

Hydrogen. Approximately all of the available data are based on a pressure of approximately 1 atm and cover a temperature range from approximately —257 C to 825 C. The average values for 1 atm pressure and various temperatures are shown by the curve in Fig. 1. Some data are reported for a pressure of approximately $^1/_2$ atm for a temperature range of —250 C to 20 C. In general, good agreement exists between the data of the various investigators.

Considerable data relative to the thermal conductivity of hydrogen are available for a pressure of 1 atm and a temperature range from —250 C to 100 C. Serious disagreement exists for the various data at any given temperature within the specified range. Average values have been obtained and are plotted in Fig. 2.

Mercury. Few data are available relative to the dynamic viscosity of mercury. All of the experimental values are for a pressure of approximately 1 atm and a temperature range from 220 C to 610 C. The data of the various investigators agree fairly well. The curve in Fig. 1 represents average values.

Except for the work of Schleiermacher (19), no experimental investigations dealing with the thermal conductivity of mercury vapor were found in the literature. In the reference cited a value of 77.2 (10^{-6}) Joule/cm sec C is given for a temperature of 203 C. It is obvious that a great deal of experimental work is required in order to obtain additional data relative to mercury.

Nitrogen. A number of investigators have determined the dynamic viscosity of nitrogen at atmospheric pressure for temperatures ranging from —100 C to 1400 C, and the agreement between the various investigators is satisfactory. Average values for the existing data are represented by the curve in Fig. 1.

Several researchers (95, 125, 130) have studied both the effect of pressure and temperature on the dynamic viscosity of nitrogen and the data agree within about 4 per cent.

Considerable data are available relative to the thermal conductivity of nitrogen. At a pressure of 1 atm values are reported for a temperature range from —193 C to 100 C. These data when plotted show considerable scattering in the temperature range from —50 C to 100 C. The curve in Fig. 2 represents average values.

Fritz (116) presented results which show the influence of pressure on the thermal conductivity of nitrogen. The pressure and temperature ranges for this work are approximately 1 atm to 97 atm and 40 C to 60 C, respectively. For a temperature of 40 C, the thermal conductivity increased approximately 19 per cent for a pressure increase of approximately 97 atm. The increase in thermal conductivity with pressure for a given temperature was found to be nearly linear.

Oxygen. All of the available data for the dynamic viscosity of oxygen are referred to a pressure of approximately 1 atm and for temperatures ranging from —191 C to 829 C. The agreement in data is satisfactory. Average values for the data are shown by the curve in Fig. 1.

Data are available for the thermal conductivity of oxygen for a pressure of 1 atm and temperatures ranging from —193 C to 100 C. In general, good agreement exists for the available data. Average values for the temperature range specified have been plotted in Fig. 2.

Steam. Many workers have conducted investigations in an effort to determine the viscosity of superheated steam over a wide range of pressures and temperatures. The serious lack of agreement between the various data was brought out in a recent paper (133) in which comparisons of the data at various pressures and temperatures are shown. Average values for the viscosity of steam for a pressure of 1 atm have been plotted in Fig. 1.

A number of experimental and theoretical studies have been made relative to the thermal conductivity of superheated steam. Values have been reported for pressures up to 290 atm and temperatures of 550 C. The serious disagreement between the results of the various investigations is clearly shown when the various data are compared. A discussion of the data on the thermal conductivity of steam was recently presented by Rudorff (132).

CONCLUSIONS

The review of the available data on the dynamic viscosity and thermal conductivity of the twelve gases indicates a critical need for additional experimental work. Examination of Figs. 1 and 2 shows that there is a serious lack of information in the range of temperatures and pressures encountered in engineering work.

The lack of data and in some cases disagreement in results are not surprising when one considers the enormously difficult problems which confront experimenters pursuing research work dealing with the determination of the thermal conductivity and viscosity of gases and vapors at elevated pressures and temperatures. The problems encountered in the design of apparatus for high-pressure and temperature research are many and varied, and are often extremely difficult to solve.

Before World War II, the engineers to a large extent relied on the basic research work of the European institutions to provide data on the thermal conductivity and viscosity of gases and vapors. The data from these organizations will in all probability not be forthcoming in the immediate future at the same rate as in the past; hence every effort should be made to encourage engineers and scientists in this country to pursue research work dealing with these properties.

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Industry's Requirements for Data on Gas Properties

By N. A. Hall,[1] Minneapolis, Minn.

A broad survey has been made among industries for which data upon the properties of the gases treated in this series of papers are of great importance. The requirements specified, which are being submitted to the ASME Special Research Committee, will be of great aid in formulating the research program. Full co-operation in the work to be undertaken will be supplied by industry and Federal agencies.

The physical and thermodynamic properties of gases are among the tools used by mechanical engineers in many exact calculations. Standard tables of data on these properties summarize available knowledge of these tools which permits them to be used to advantage. As design requirements have become more exacting, however, it is apparent that our knowledge of these basic data is often inadequate. The accuracy of any analysis depends upon the reliability of the standard reference data employed, and industry has a continuing requirement for more basic data to satisfy its increasing needs in this respect.

This problem is not confined to any one industry or any one set of engineers. In response to a general demand, therefore, the ASME Special Research Committee on Properties of Gases and Gas Mixtures has undertaken to co-ordinate industry's requirements in this field as a preliminary step in organizing its proposed program of research. Fortunately, representatives from many industries have been among the sponsors of this activity, and a number of these representatives have been prominent in the work of the committee to date.

In order to have at hand a comprehensive picture of the current and prospective needs of industry, the committee has sponsored a survey which endeavored to cover the field as fully as possible. From a review of the replies, three definite observations can be made.

1 The needs for data on gas properties are varied and comprehensive; the contemplated program of research cannot afford to specialize on any small number of gases.

2 The set of standard reference data to be established should be arranged so that it can grow and be revised continually as additional authoritative data become available.

3 The need for data on gas mixtures is of major importance; few such data are available, and experience has shown that the properties of some of the more common mixtures cannot be calculated reliably from the known properties of their components.

Industries Consulted

Gas properties are involved in almost every industry requiring mechanical-engineering techniques, so that it has been necessary to approach a large number of organizations. In addition to the field of mechanical engineering, chemical engineering will have a major interest in this work. Petroleum refining, which has been called the largest chemical industry in the world, has as extensive a need for gas-properties data as any. In recognition of this fact, the American Petroleum Institute has been sponsoring at the National Bureau of Standards its Research Project 44 on the collection and evaluation of data on the thermodynamic properties of hydrocarbons, and the basic gases, oxygen, nitrogen, hydrogen, CO, and CO_2. The director of this project at the Bureau of Standards, Dr. F. D. Rossini, is also a member of the ASME Special Research Committee, and a veryclose liaison between these two activities is to be expected. In connection with the work of the API project, it may be noted that replies received from the petroleum industry in the present survey indicate a need for high-pressure thermodynamic properties and for data on process gases not included in the API program.

The chemical industry, including gas processing and handling, also has widely varied requirements. One of the greatest needs here is adequate information on mixtures of even some of the more common gases, such as oxygen and nitrogen.

Although the refrigeration and air-conditioning industry has been established for many years, current developments in this field are characterized by an increasing amount of engineering refinements. The wide use of newer and specialized refrigerants calls for many extensive data to determine optimum utilization. One can easily list twenty-five or more gases used as refrigerants of which at least one half have their major application in this industry.

In power development the manufacturers of steam and gas turbines, the railroads, and the aircraft industry are refining their designs, going to higher pressures and introducing new working substances. Each of these changes requires much more information on gas properties.

While these represent the industries most concerned, the Federal Government, as a major service agency and also consumer, sets the standards for many requirements. Accordingly, contact has been made with the Bureau of Standards, the Bureau of Mines, the National Advisory Committee for Aeronautics, the Office of Naval Research, the Navy Department, Bureau of Ships, and the War Department, Division of Research and Development. The needs reported by these agencies are extensive but specific. They call for information to aid in the design of power plants and propulsion systems, to enable more comprehensive study of combustion, to provide more reliable design in gas-handling and storage, among many other problems.

Questions Considered

In conducting this survey, a brief statement of the nature and pertinence of the project was submitted to each individual representing a particular industry or service group. In preparing information to be submitted, it was suggested that the following items be considered:

1 The relative importance of the several technical gases.

2 The relative importance of the several thermodynamic and physical properties.

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Contributed by the Applied Mechanics and Heat Transfer Divisions, under the auspices of the Research Committee on Properties of Gases and Gas Mixtures, and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-169.

3 The accuracy desired for data.
4 The form of tables and charts for presenting technical data.

In reviewing the replies received from these groups, it was obvious that the needs of industry are remarkably varied. At least 75 specific gases or gas mixtures were mentioned, of which almost one half were considered to be of major importance by at least one individual.

PRIORITY OF INTEREST

The individual gases mentioned may be summarized in groups which will be discussed in somewhat more detail, arranged in the general order of priority in Table 1, together with their more important properties.

TABLE 1 IMPORTANT GASES TO BE CONSIDERED AND THEIR PROPERTIES

1	Basic gases	5	Inert gases
2	Hydrocarbons	6	Dissociated gases
3	Gas mixtures	7	Minor atmospheric gases
4	Refrigerants and process gases	8	Propulsion gases

Thermodynamic Properties

	Major		Minor
1	Constant-pressure specific heat	1	Vapor pressure
2	Constant-volume specific heat	2	Heat of vaporization
3	Internal energy	3	Joule-Thompson coefficient
4	Enthalpy	4	Acoustic velocity
5	Entropy	5	Entropy of vaporization
6	Compressibility or p-v-T	6	Critical constants

PHYSICAL PROPERTIES

	Major		Minor
1	Viscosity	1	Kinematic viscosity
2	Thermal conductivity	2	Prandtl number
3	Emissivity	3	Diffusivity

CHEMICAL THERMODYNAMIC PROPERTIES

	Major		Minor
1	Free energy	1	Fugacity
2	Heat of formation	2	Dissociation equilibrium constant
3	Free energy of formation		

Other gases were mentioned which were of specialized importance or were readily derivable from those listed. Generally, the six major thermodynamic and the three major physical properties appear to form a minimum set of requirements.

For further detail it is convenient to examine the situations with regard to the several gas groups mentioned in Table 1.

The basic gases appeared to be of primary importance in almost every case. Included are oxygen, nitrogen, water vapor, carbon dioxide, hydrogen, and carbon monoxide. While the zero-pressure thermodynamic properties of these gases are of primary importance, developments in high-pressure processes and storage require more information on compressibilities up to at least 3000 psia with accuracies up to three significant figures. However, at high temperatures up to 6000 deg R, combustion problems generally appear not to require data at pressures of over 10 to 15 atm. Recent developments in gas-handling and separation have called for properties of these basic gases in the vapor state. It appears that industry's top priority should be assigned to securing data for this group of the greatest possible accuracy, for a range of temperatures from well below the critical up to 6000 deg R, and for pressures up to at least critical at low temperatures, to several thousand psia at moderate temperatures, and somewhat less at extreme temperatures.

The group of hydrocarbons, while primarily of interest to the petroleum industry, is so widely used that its properties should be exhaustively considered. The immediate specific needs of the petroleum industry are being met by the API Project 44. In general, mention has been made of the need of additional compressibility and vapor-phase data. Specific compounds for which such data are lacking include the pure and oxygenated hydrocarbons through the C_4 range.

While in many cases it was indicated that reasonably adequate data for pure gases were at hand, frequent reference was made to a serious lack of information on mixtures of gases. Many operations in petroleum-refining, gas separations, and combustion, t mention only a few, involve a great variety of mixtures. Since i only a few cases, such as air, is it possible to refer to a mixture o fixed composition, it is evident that either much more extensiv tables must be provided, or adequate methods of computing properties of mixtures from components must be developed. Fo some of the more common binary mixtures, such as oxygen-nitrogen, nitrogen-methane, carbon monoxide-water vapor, and probably several others, the first procedure will be justifiable. In general, however, the investigation of analytical methods appear to be particularly urgent.

While the first three groups are of universal importance, the remaining groups are in most cases of specialized interest. The need for data, however, is frequently very severe. The group o refrigerants and process gases has become very extensive. Included are the chlorinated and fluorinated hydrocarbons, ammonia, the sulphur gases, SO_2 and H_2S, chlorine, fluorine, mercury vapor, and others. In many cases properties of these gases have been obtained by the industry most concerned. For these, the thermodynamic, physical, and thermochemical properties are al fairly equally important. For refrigerants the vapor-liquid properties are of course most needed. Moderate accuracy on the order of two to three significant figures is desired. This group illustrates perhaps better than others the need for consistent authoritative data. In too many cases the information available has been developed to meet specialized need so is very limited in scope.

Inert gases form a consistent group which includes helium argon, neon, krypton, xenon, and radon. Of these, helium is important to industry because of its unique physical and chemical properties and because of its availability. Argon is of interest primarily because it is a significant component of air. Neon has some slight use, while the others have negligible engineering application. Fairly complete data on helium are called for to facilitate its handling and to evaluate potential power or process uses Sufficient data on argon are required for proper analysis of air properties and of other oxygen-nitrogen-argon mixtures.

In all combustion involving technical gases, in many chemical processes, and in all operations at extreme temperatures, significant quantities of dissociated gases will occur. Included are primarily atomic oxygen, hydrogen, and nitrogen, hydroxyl, OH and others such as NH, CH, and CN. Since these occur most frequently in high-temperature reactions, there is greatest need for low-pressure thermodynamic and chemical properties, including dissociation energies. Data are needed from room temperatures to at least 6000 deg R and higher if possible. Accuracy should be the same as that available for the basic gases.

In certain specialized applications in aeronautics and combustion, various minor atmospheric gases are of importance. Chief among these are ozone and the oxides of nitrogen. The properties of most importance will depend upon the use, but should include the major thermodynamic and physical properties at a minimum.

The final group, identified as propulsion gases, includes certain vaporized metal oxides, fluorides, carbides, and nitrides, particularly Li_2O, Al_2O_3, B_2O_3, MgO, BF_3, AlF_3, and LiF. These have come into importance largely in military propulsion developments, and there appears to be an almost total lack of data. Most needed are thermodynamic properties at extreme temperatures.

In regard to accuracy, it is difficult to draw the line between the need for ultimate reference data and the advisability of meeting broad requirements. One individual writes that it would probably be more profitable to obtain data on a large number of pure materials and mixtures over a wide range of conditions with an accuracy of plus or minus 2 per cent rather than concentrate on extremely accurate data over a limited range of conditions. Another, however, states specifically the belief that the efforts of the special research committee should be directed toward obtaining data of the highest feasible degree of accuracy. It appears that a compromise insuring breadth of investigation with the least possible sacrifice in quality is in order.

ACKNOWLEDGMENT

The foregoing cannot possibly do justice to the extensive store of information furnished so willingly by industry ond the government agencies. The replies received and considered in this review include a number of carefully planned and detailed program suggestions outlined by the directors of research in various organizations consulted. These replies will be submitted to the committee, and the present summary can indicate only the general scope of the requirements. If interest and co-operation will assist the work of the ASME special research committee, the evidence given in this correspondence should insure a strong and useful program.

Facilities for, and Work Under Way in Gas-Properties Research

By R. V. KLEINSCHMIDT,[1] STONEHAM, MASS.

The Subcommittee on Research Planning of the Research Committee on Properties of Gases has made a survey of laboratories believed to be interested in research on gas properties, to determine (1) work completed, (2) work in progress, (3) facilities and experienced personnel available but not now utilized, and (4) other laboratories that might be interested in developing such equipment and personnel.

IN order to make the compilation of data on the properties of gases as simple as possible, especially for the laboratories contacted, a tabular questionnaire (see following page), which appears to have been as satisfactory as any such simplified form could be, was sent to a selected list of laboratories. Each recipient was also asked to suggest others who should be contacted. In this way, a total of 40 laboratories were contacted, and 26 replies were received. Many of the replies were supplemented by letters and reprints, describing more fully the situation and facilities. Therefore the subcommittee has an extensive amount of information of which this paper is a general summary.

The subcommittee wishes to express its appreciation of the high degree of co-operation from those who supplied the basic data.

The committee's interest is divided into two fields:

1 Thermodynamic properties, i.e., enthalpy as a function of pressure and entropy. This necessarily includes such data as specific and latent heats, specific volume, adiabatic exponent, k, etc.

2 Mechanical-thermal properties, such as viscosity, thermal conductivity, thermal radiation, and absorption, etc. These are primarily of interest in the field of heat transfer and flow.

Determination of the thermodynamic properties can be accomplished in a variety of ways which furnish valuable cross-comparisons and checks. Probably the simplest and most accurate method is to determine the "perfect gas" specific heat, $C_p = (dH/dT)_p$ (at very low pressures), from spectroscopic measurements (in the case of the simpler molecules), or from direct calorimetric measurement in the case of complex molecules, or of chemically reactive mixtures, and then to determine the variation of enthalpy with pressure by some form of Joule-Thomson measurement, either adiabatic, $(dT/dP)_H$, or isothermal, $(dH/dP)_T$. These two types of measurement together with specific volume measurements will give all the data required for a complete thermodynamic description of the properties of a gas as pointed out by H. N. Davis.[2] Other useful data as checks, or to cover pressure and temperature ranges, where direct measurements are not possible, include measurements of specific and latent heats, and velocity of sound.

The survey showed that much attention is being devoted to the spectroscopic determination of the perfect gas, or zero-pressure specific heats over a wide range of temperatures. Ten laboratories reported work in progress and two others appeared interested in the field. Very little work is in progress in Joule-Thomson data required to determine deviations from the perfect gas laws at high pressures. Four laboratories had done such work, two have work in progress, and two are interested in such work. However, almost all of this work is at relatively low temperatures and pressures.

In the mechanical-thermal field, the situation is also not entirely satisfactory. Work on viscosity at four laboratories and work on thermal conductivity at three is going forward, but there is an urgent demand for more and better data of this nature for heat-transfer calculations.

It is especially interesting to note that through the vigorous efforts of the API, extensive programs on hydrocarbon gases are under way, which account for over half the total activity in gas-properties measurements.

Exclusive of the hydrocarbon gases, there are some sixteen gases considered by the committee to be of immediate general interest, and many others are of interest to certain industries. An indication of the magnitude of the effort required to obtain the necessary data can be had from the fact that three of the best laboratories in the country financed by the ASME Steam Properties Committee, spent from 4 to 10 years each to bring our knowledge of the properties of steam alone to its present state. Even now, further work at extreme pressures and temperatures is needed.

SUMMARY

The survey showed that there is urgent need for increased interest in gas-properties research, especially in Joule-Thomson measurements at high pressures and high temperatures. Additional work on viscosity, thermal conductivity, and thermal radiation is also required.

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[1] Consulting Engineer. Mem. ASME.

Contributed by the Applied Mechanics and Heat Transfer Divisions, under the auspices of the Research Committee on Properties of Gases and Gas Mixtures, and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-170.

[2] "The Value of Joule-Thomson Observations for Computing Steam Tables," by H. N. Davis; *Physical Review*, vol. 5, 1915, p. 359.

QUESTIONNAIRE ON THERMAL PROPERTIES OF GASES AND GAS MIXTURES

Name . . . .

Address . . . .

Using alphabetical legend please fill in table given below:

(A) Work completed and published (Please give reference)
(B) Work in progress and some results available
(C) Work started but no results
(D) Work planned but not yet started
(E) Equipment available but lack manpower or funds
(F) Experienced supervision available but lack manpower or funds
(G) Interested in subject but no specific qualifications

Properties	Temperatures, deg Kelvin					Pressures, atmospheres			
	80	80-270	270-400	400-800	800-	0-1	1-10	10-100	100-
Experimental:									
Spectroscopic Data									
P-V-T Data									
Specific Heats (Calorimetric)									
Joule-Thomson Data									
Velocity of Sound									
Equilibrium Data									
Viscosity									
Thermal Conductivity									
Critical Data									
Computations:									
Spectroscopic									
Formulations									
Enthalpy and Entropy									

Questionnaire, Properties of Gases

Please comment on your work on any of the following gases:

Argon, He, N_2, O_2, H_2, H_2O, CO_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, NH_3, N_2O, NO, NO_2, SO_2, SO_3, H_2S, and other gases.

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Please indicate institutions which should be approached in addition to those listed below:

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This questionnaire is being sent to the following:

(1) The Ohio State University
(2) National Bureau of Standards
(3) Georgia Institute of Technology
(4) Massachusetts Institute of Technology
(5) The Pennsylvania State College
(6) National Research Council, Canada
(7) University of Wisconsin
(8) Washington University, St. Louis
(9) The Johns Hopkins University, Applied Physics Laboratory
(10) California Institute of Technology
(11) U.S. War Dept., Research & Develop. Sub-office of Chief of Ordnance, California Institute of Technology
(12) California Institute of Technology, Jet Propulsion Laboratory
(13) Illinois Institute of Technology
(14) Leland Stanford University
(15) University of California at Los Angeles
(16) Carnegie Institute of Technology
(17) University of Pittsburgh
(18) Yerkes Observatory, University of Chicago

Generalized Thermodynamics of High-Temperature Combustion

By H. C. HOTTEL,[1] G. C. WILLIAMS,[2] and C. N. SATTERFIELD[3]

The ability to calculate the performance of any proposed type of heating operation or power-plant combustion cycle requires a knowledge of the thermodynamic properties of the system. If the systems encountered consist of any combination of the four species, carbon-hydrogen-oxygen-nitrogen, in any reasonable proportion, the number of thermodynamic charts necessary for a solution with minimum interpolation would be enormous without specially developed procedures. This paper presents a method of expressing the thermodynamic properties of the four-component system in a dimensionless form which permits putting the whole system onto a simple set of charts for easy engineering use. The present data have particular value in calculating flame temperatures and in solving the performance of liquid-fuel rocket power plants. The data span the range of operation of conventional combustion systems and therefore also apply to systems such as furnaces operated with oxygen enrichment or very high preheat, as well as most usual power cycles. The method of use is illustrated by application to a rocket system.

Nomenclature

The following nomenclature is used in the paper:

H = enthalpy, above CO_2, H_2O (vapor), O_2, and N_2 at 0 deg absolute

$H_{14.7}$ = value of enthalpy at 14.7 psia

H_{300} = value of enthalpy at 300 psia

H_f = fictitious enthalpy, based upon simplified gas composition. For a fixed temperature, H_f does not vary with pressure (see text)

$H_{f,0}$ = value of H_f at 0 deg K

$H_{f,2400}$ = value of H_f at 2400 deg K

$H_{red,14.7} = \dfrac{H_{14.7} - H_{f,0}}{H_{f,2400} - H_{f,0}}$

$H_{red,300} = \dfrac{H_{300} - H_{f,0}}{H_{f,2400} - H_{f,0}}$

S = entropy, Btu/lb deg R, above CO_2, H_2O (vapor), O_2, and N_2 at 0 deg absolute, and each at 14.7 psia

$S_{14.7}$ = value of entropy at 14.7 psia

S_{300} = value of entropy at 300 psia

S_f = fictitious entropy, based upon simplified gas composition; for a fixed temperature S_f does not vary with pressure (see text)

$S_{f,2400}$ = value of S_f at 2400 deg K

$S_{red,14.7} = \Delta_{14.7} + S_{14.7}/S_{f,2400}$

$S_{red,300} = \Delta_{300} + S_{300}/S_{f,2400}$

$\Delta_{14.7}$ = an empirical quantity added to $S/S_{f,2400}$ to cause all values of $S_{red,14.7}$ to coincide at $T = 2000$ deg K

Δ_{300} = empirical quantity added to $S/S_{f,2400}$ to cause all values of $S_{red,300}$ to coincide at $T = 2400$ deg K

$\Delta_{14.7}$ and Δ_{300}, each varies with the atom-ratio combination but not with the temperature.

Note: Above 1600 deg K, true equilibrium is assumed. Below 1600 deg K, the composition is assumed to be the same as at 1600 deg K.

Introduction

The increasing interest in high-output or high-temperature combustion processes, involving special fuels or oxygen enrichment, emphasizes the desirability of a method of handling the problem of predicting performance which is free from the tedious procedure associated with calculation of thermodynamic equilibrium composition. Rocket power plants constitute a good example of the need; evaluation of their performances is often long and tedious, requiring the solution of several simultaneous algebraic equations, usually by trial-and-error techniques, to obtain an answer for one given operating condition. When the optimum operating conditions are to be determined or several fuel-oxidant systems studied, the time and effort required are often very considerable. Several thermodynamic-property charts have been prepared which greatly reduce the work required in solving problems in internal-combustion and other motors, using hydrocarbon fuels with air as the oxidant (1–10 inclusive).[4] Each of these charts treats one particular atomic composition corresponding to a fuel mixture of interest. In order to cover a range of atomic compositions with one or a few charts, various other techniques have been suggested (11, 12, 13, 14); all of these, however, involve the use of simplifying assumptions which introduce a substantial error.

The object of this study was to prepare a set of generalized thermodynamic data which encompass all probable compositions of interest of the four-component system, carbon-hydrogen-oxygen-nitrogen, and which have particular value in calculating flame temperatures and solving problems of performance of liquid-fuel rocket power plants. The data also span the range of operation of conventional combustion systems and therefore also apply to systems such as furnaces operated with oxygen enrichment or very high preheat.

These generalized data present the properties of various ratios of carbon, hydrogen, nitrogen, and oxygen in chemical equilibrium at temperatures up to 3200 deg K, and at two pressures; 14.7 and 300 psia. They may be used in solving problems involving chemical species which are composed of any two or more of these elements in almost any proportions. The ratios considered include those which are encountered with mixtures of fuels such as hydrogen, gasoline, alcohols, ammonia, organic amines, and hydrazine; and oxidants such as oxygen, air, hydrogen peroxide, and nitric acid. By means of these data, rapid determinations

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[3] Assistant Professor of Chemical Engineering, Massachusetts Institute of Technology.

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and ont those of the Society. Paper No. 47—A-21.

[4] Numbers in parentheses refer to the Bibliography at the end of the paper.

may be made of adiabatic flame temperature at 14.7 or 300 psia, and available work or heat from any power or heating cycle working within these limits. Interpolation between or extrapolation beyond these limits is possible with not too great error.

Bases for Thermodynamic Functions

A value of zero for the entropy, enthalpy, and internal energy was assigned to each of the products of complete combustion at 1 atm pressure and 0 deg K, namely, CO_2, H_2O (vapor), O_2, and N_2. The value of the thermodynamic function of each chemical species is usefully divided into two parts, a "sensible" portion, and a "chemical" portion. The sensible portion is the change in value on cooling without change in state or composition to 0 deg K. To this is added the change in value on complete combustion at 0 deg K, to form CO_2, H_2O (vapor), O_2, and N_2, at 1 atm pressure. For example, the enthalpy of CO at 300 deg K is equal to the heat evolved on cooling the CO to 0 deg K at constant pressure, plus the heat evolved on combustion to form CO_2 at 0 deg K. This calculation is made without regard to whether there is sufficient oxygen to complete the combustion, since O_2 introduced at 0 deg K adds nothing to H, S, or E, as just defined.

The dead state at 0 deg K and 1 atm is the hypothetical gaseous state commonly used as a base. The thermodynamic functions with this base therefore do not include the contributions of vaporization, or freezing, or of imperfect-gas behavior. These omissions are justified since these charts are for use in regions where all the constituents are gaseous and where deviations from perfect-gas behavior are small.

Since the rate of chemical reaction becomes very slow at temperatures below 1600 deg K, and since most practical problems involve rather rapid processes, the composition of gas mixtures below 1600 deg K is considered to be "frozen" at the equilibrium value for 1600 deg K. This mixing of thermodynamics and reaction rates has a reasonable basis in experimental data.

Since dissociation is negligible at 1600 deg K (except for very low pressures), usually only the water-gas equilibrium is involved in the stated assumption. Since the heat of this reaction is small, the values of the thermodynamic functions below 1600 deg K do not deviate greatly from those which would be calculated assuming chemical equilibrium did exist.

Calculation Procedure

Seventy-nine combinations of the ratios of the elements carbon, hydrogen, nitrogen, and oxygen were chosen which covered the probable regions of interest. Each combination was expressed in terms of the atomic ratio of carbon to oxygen C/O, hydrogen to oxygen H/O, and nitrogen to oxygen N/O. For each atom-ratio combination, the equilibrium gas composition was calculated for values of the temperature at 200 deg K intervals between 1600 deg K and 3200 deg K, and at two pressures, 14.7 and 300 psia. The maximum temperature studied at 14.7 psia was 3000 deg K. The equilibrium composition of the gas mixture was calculated by conventional means, involving the solution of several simultaneous algebraic equations which expressed the equilibrium relationships and material balances involved. When the composition has been found, calculation of the internal energy, enthalpy, entropy, and volume or molecular weight of the mixture is straightforward.

Presentation of such results in the form, for example, of temperature-enthalpy diagrams would be objectionable from the standpoint of the enormous number of curves necessary to represent an adequate number of composition ratios in the four-component system C–H–O–N. Therefore some generalized method of presentation was sought.

In preparing generalized (or reduced) data, there exists the problem of balancing ease of use against accuracy in use in their presentation. Thus it is highly desirable for accurate interpolation to use functions of enthalpy and entropy which cause the data for the wide range of gas compositions to lie as close to a common curve as possible, but yet not make the functions so complicated that the advantage of rapid calculation is considerably nullified.

Use of the enthalpy function ($H\text{-}H_0$), gives the various curves a common point at 0 deg K, but still leaves a wide spread at the higher temperatures. These curves may be brought together more closely at the higher temperatures and given another common point by dividing this function by $H_T\text{-}H_0$, where T is some arbitrarily chosen temperature in the mean range of interest. The curves will now have a second point at T.

It is also important that some means be provided for easily computing H_T and H_0 for the element ratios representing any given fuel-oxidant mixture. Such a means has been developed in a set of simple rules which will be given. These rules permit the rapid calculation of a fictitious gas composition from which values of a fictitious enthalpy at 0 deg K, ($H_{f,0}$) and at T deg K ($H_{f,T}$) may be calculated; these fictitious enthalpies are found to bring the generalized H-curves together at 0 deg and T deg substantially as well as the true enthalpies would.

The temperature picked for the second tie point was 2400 deg K (4320 deg R). This temperature is sufficiently high to be in the region of particular interest in combustion problems, yet not so high that an appreciable amount of dissociation occurs at pressures of 14.7 psia and above. Thus the real gas composition may be approximated closely in this region of temperature and pressure by the simple fictitious gas composition which does not include dissociated products.

Summarizing, a dimensionless enthalpy ratio or reduced enthalpy H_{red} is obtained, defined as follows

$$H_{\text{red}} = \frac{H - H_{f,0}}{H_{f,2400} - H_{f,0}}$$

in which

H = true enthalpy of mixture, above CO_2, H_2O (vapor), O_2, N_2 at 0 deg K

H_f = fictitious enthalpy, or enthalpy of a fictitious mixture having the same atomic composition as the actual mixture in question, but having a simpler molecular composition. H and H_f must of course refer to the same mass of mixture (see following text)

$H_{f,0}$; $H_{f,2400}$ = values of H_f at 0 deg K and 2400 deg K, respectively. It is to be noted that $H_{f,0}$ and $H_{f,2400}$ are both calculated from the one fictitious gas composition.

Values of the function H_{red} are plotted versus temperature in Figs. 1 and 2, for the two pressures of 300 and 14.7 psia.

In an analogous manner, a reduced internal energy E_{red}, may be defined and used. No values of this function are presented in the present paper.

The need for a readily calculable gas composition to use instead of the true composition in forcing a similarity of H-curves for different atomic-mixture ratios has been emphasized. In this fictitious composition the only components considered are alternatively:

(1) CO_2, O_2, H_2O, N_2, if the mixture contains less than the stoichiometric quantity of fuel,

(2) CO_2, H_2O, N_2, if the mixture contains the stoichiometric quantity of fuel,

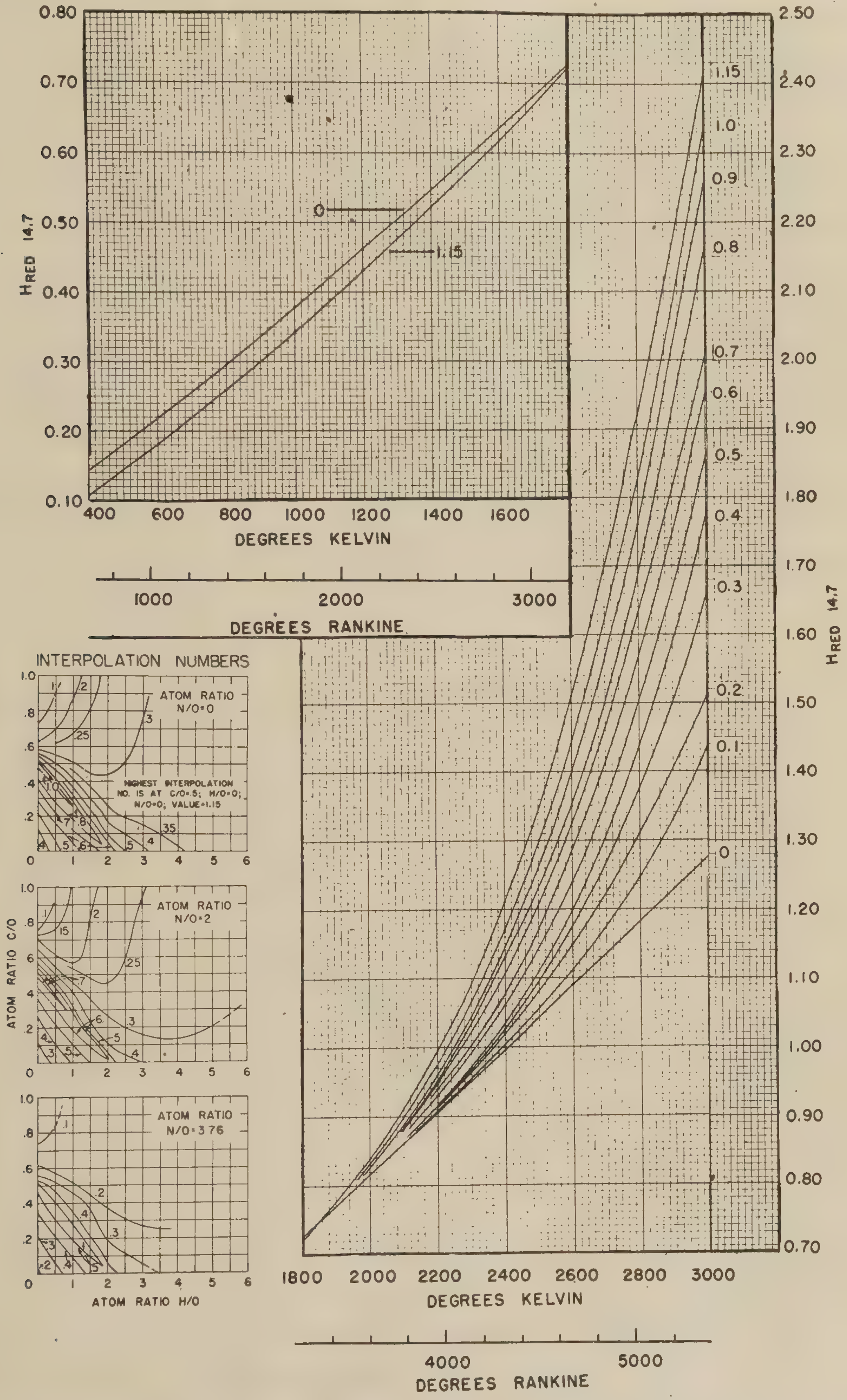

Fig. 1 Generalized Temperature-Enthalpy Relation for System C–H–O–N in Thermodynamic Equilibrium at 300 Psia

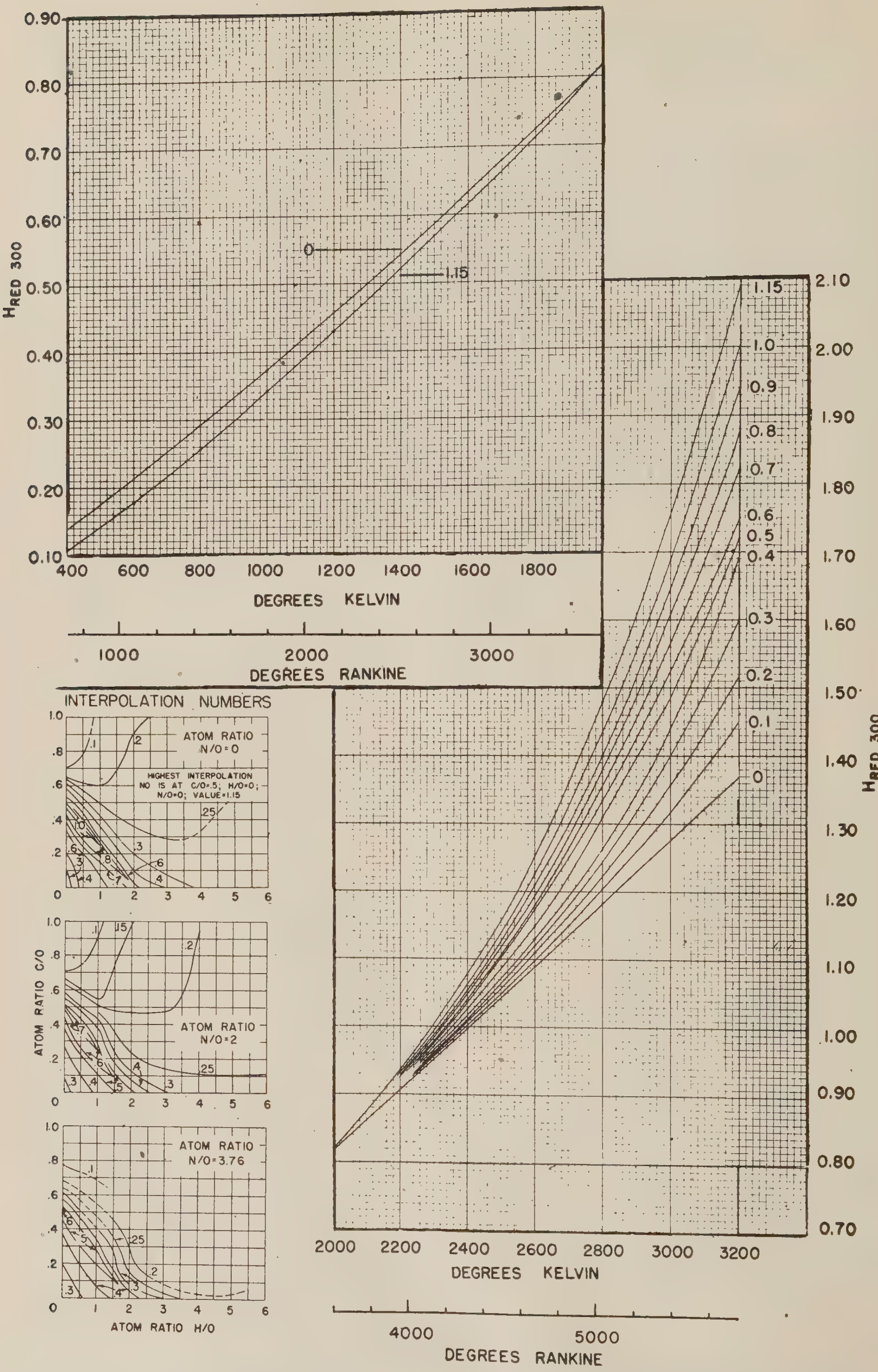

Fig. 2 Generalized Temperature-Enthalpy Relation for System C–H–O–N in Thermodynamic Equilibrium at 14.7 Psia

(3) CO_2, CO, H_2O, N_2, if the mixture contains more than the stoichiometric quantity of fuel.

If a system falls in the first or second category, the fictitious composition is easily calculated by simple material balances. If it falls in the third, an additional relationship is needed. Assumption of equilibrium among the four components of the "water-gas" reaction provides the needed relation. Empirically, it has been found that a satisfactory fictitious composition is obtained by using a constant value of 4.78 for the water-gas equilibrium constant. The resulting relation is presented graphically in Fig. 5, which gives the fraction of total carbon present as CO_2. With CO_2 and CO determined, an oxygen balance indicates the amount of the hydrogen present as water.

Note that the shaded area in the lower left-hand corner of Fig. 5 represents atomic compositions for oxidant-rich systems. In this region the water-gas equilibrium does not occur, and all the carbon is present as CO_2.

With fictitious gas composition calculated, $H_{f,0}$ and $H_{f,2400}$ may be calculated by use of Table 1. Any consistent system of units may of course be used.

TABLE 1 VALUES OF ENTHALPY AND ENTROPY OF COMBUSTION PRODUCTS

	H_0 Btu/lb-mol	H_{2400} Btu/lb-mol	S_{2400} Btu/lb-mol deg F
H_2........	102794	135218	46.544
H_2O.......	0	44689	65.60
CO........	120184	154620	63.504
N_2.........	0	34146	61.83
O_2.........	0	35779	65.90
CO_2.......	0	54031	76.63

The determination of H_{red} raises the question of interpolation to allow for atomic composition of the mixture. At any particular high temperature, say, 3000 deg K, the value of H_{red} is found to vary from a maximum for the atomic-composition ratio $C:H:O:N = 1:0:2:0$ to a minimum for the ratio $C:H:O:N = 1:0:1:0$. If at some fixed temperature the possible range of values of H_{red} is divided into steps of arbitrary equal size, and identification numbers (referred to later as interpolation numbers) are assigned to these values, various atomic compositions will correspond to each value of H_{red}, and lines of equal H_{red} may be drawn on a composition diagram. Such lines appear on three small plots at the bottom left of the main $T - H$ diagrams in Figs. 1 and 2.

Composition is represented as atomic ratio of carbon to oxygen, C/O, versus atomic ratio of hydrogen to oxygen, H/O, for each of three values of atomic ratio of nitrogen to oxygen, N/O. The condition to be satisfied in order that the lines on the small diagrams be identified with the corresponding lines on the $T - H_{red}$ diagram is that the same pattern of iso-H_{red} lines (on atomic composition co-ordinates) be obtained at different temperatures. To an adequate approximation this is found to be so, e.g., if three different atomic compositions all have the same H_{red} at a particular temperature, they will also have the same H_{red} at any other temperature.

For convenience in drawing and because of the imperfect identification of any particular composition with the same interpolation number at all temperatures, Figs. 1 and 2 show all of the curves crossing at one point between 2000 and 2100 deg K. Actually, however, the curves cross at various points in a region between 2000 and 2300 deg K, and in this region some of the curves will be outside the positions indicated (by a maximum of 20 deg K).

Determination of Enthalpy of Unburned Mixture

Thermodynamic data on heats of formation and heats of combustion from the usual sources (ICT, Rossini and Bichowsky, etc.) must be converted for the present purpose to the same basis as the attached charts giving H for the equilibrium products, namely, zero enthalpy at 0 deg K in a "dead state," consisting of gaseous CO_2, H_2O, O_2, and N_2. Table 2 gives such data for a number of fuels and oxidants. Except where specified, these data represent the enthalpy of a liquid at 300 deg K (80 deg F) above the dead state at 0 deg K. The exceptions, noted in the table, are fuels or oxidants which would be gaseous at normal temperature and pressure; on the assumption that they may be used as liquids stored at atmospheric conditions and pumped into the combustion chamber, their enthalpy is evaluated assuming them liquids at their atmospheric boiling points.

Determination of Flame Temperature

The adiabatic flame temperature is that at which the total enthalpy (sensible plus chemical) of the reactants (fuel plus oxidant) equals the total enthalpy of the products of reaction. The adiabatic flame temperature is determined by entering the $H_{red} - T$ plot on the proper interpolation line with the H_{red} value calculated for the unburned mixture. If heat is transferred during the combustion process, the quantity of heat on the proper basis is added or subtracted from the enthalpy of the unburned mixture as just calculated.

Determination of Entropy S

Analogously to the enthalpy function H_{red}, an entropy function is desired which varies a minimum amount as atomic composition is changed within the four-specie system C–H–O–N. Let the true entropy be denoted as S with a numerical subscript to indicate pressure.

If, for different compositions, $S_{14.7}$ is divided by a fictitious entropy S_f evaluated at 2400 deg K on the basis of the same molecular composition assumed in evaluating H_f, it is found that the quotient $S_{14.7}/S_{f,2400}$ still varies considerably with atomic composition. However, the family of curves of $S_{14.7}/S_f$ versus T so obtained can be made to coincide at a particular temperature by vertical shifting. The amount of shifting of a curve will be called Δ, with subscript to identify the pressure. (Δ is obviously a function of atomic composition only.) The result is a plot of $(S_{14.7}/S_f + \Delta_{14.7})$, called "reduced" entropy or $S_{red,\,14.7}$, versus temperature. Two such sets of curves are given in Figs. 3 and 4, for 300 and 14.7 psia, each set carrying its associated composition-interpolation plots at the right, analogous to those used for enthalpy evaluation.

Since relative rather than absolute values of entropy are of interest in rocket calculations, it is unnecessary to know separately the values $\Delta_{14.7}$ and Δ_{300}. Knowledge of their difference is sufficient. This appears in Fig. 6 in the form of curves of constant value of $(\Delta_{14.7} - \Delta_{300})$ on composition diagrams similar to those used for composition-interpolation on H_{red} and S_{red}. Note that in any process operating between 300 psi and 14.7 psi in which the entropy changes by an amount ΔS,

$$S_{14.7} - S_{300} = \Delta S$$

$$S_{14.7}/S_f - S_{300}/S_f = \Delta S/S_f$$

Adding $\Delta_{14.7} - \Delta_{300}$ to both sides of the foregoing equations gives

$$(S_{14.7}/S_f + \Delta_{14.7}) - (S_{300}/S_f + \Delta_{300}) = \Delta S/S_f + \Delta_{14.7} - \Delta_{300}$$

from which

$$S_{red,\,14.7} - S_{red,\,300} = \Delta S/S_f + \Delta_{14.7} - \Delta_{300}$$

For a reversible process, $\Delta S = 0$.

Values for use in evaluating the fictitious entropy S_f at 2400 deg K are given for the various components in Table 1. Note that S_f by definition includes only the temperature contribution

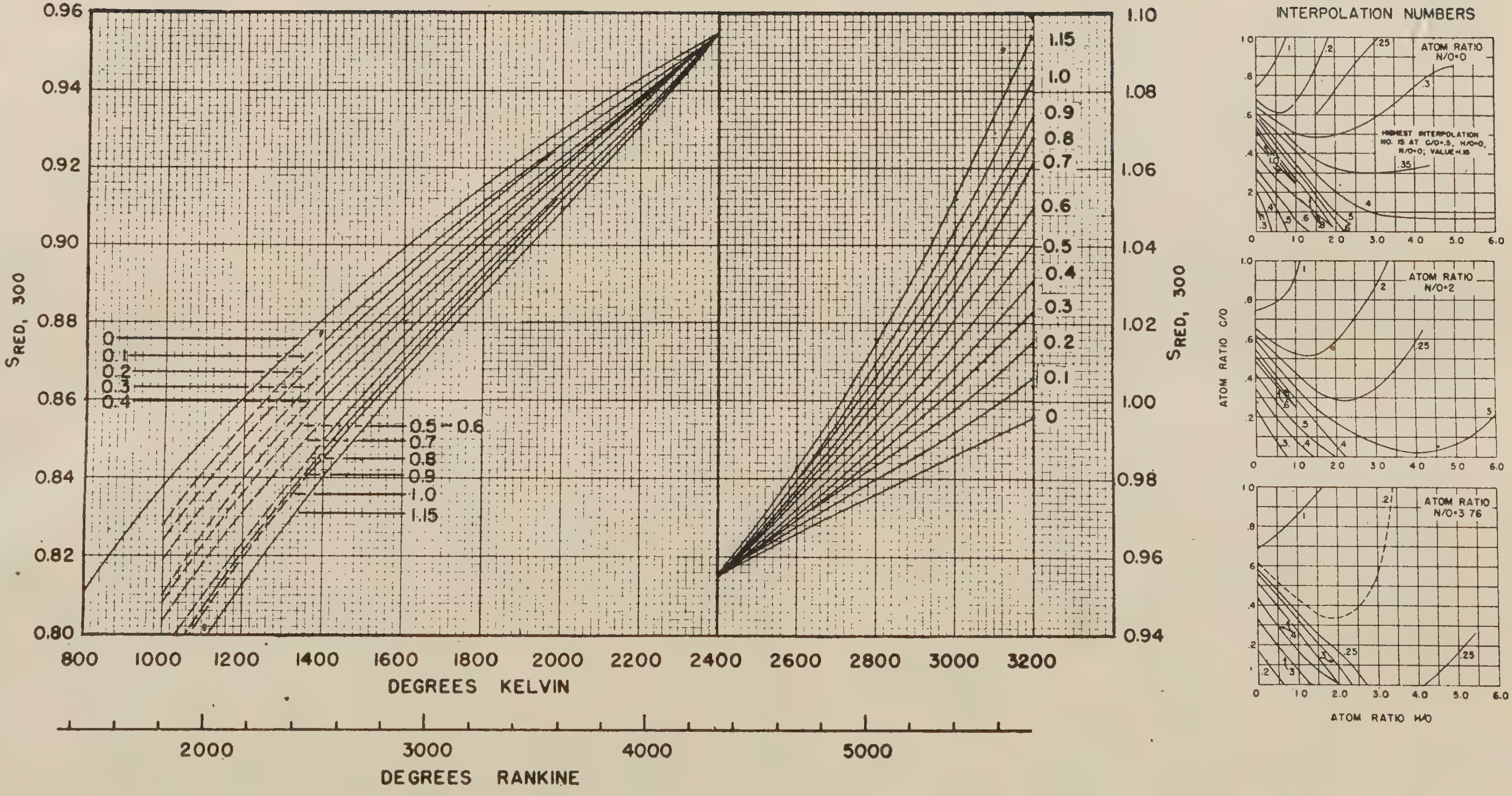

Fig. 3 Generalized Temperature-Entropy Relation for System C–H–O–N in Thermodynamic Equilibrium at 300 Psia

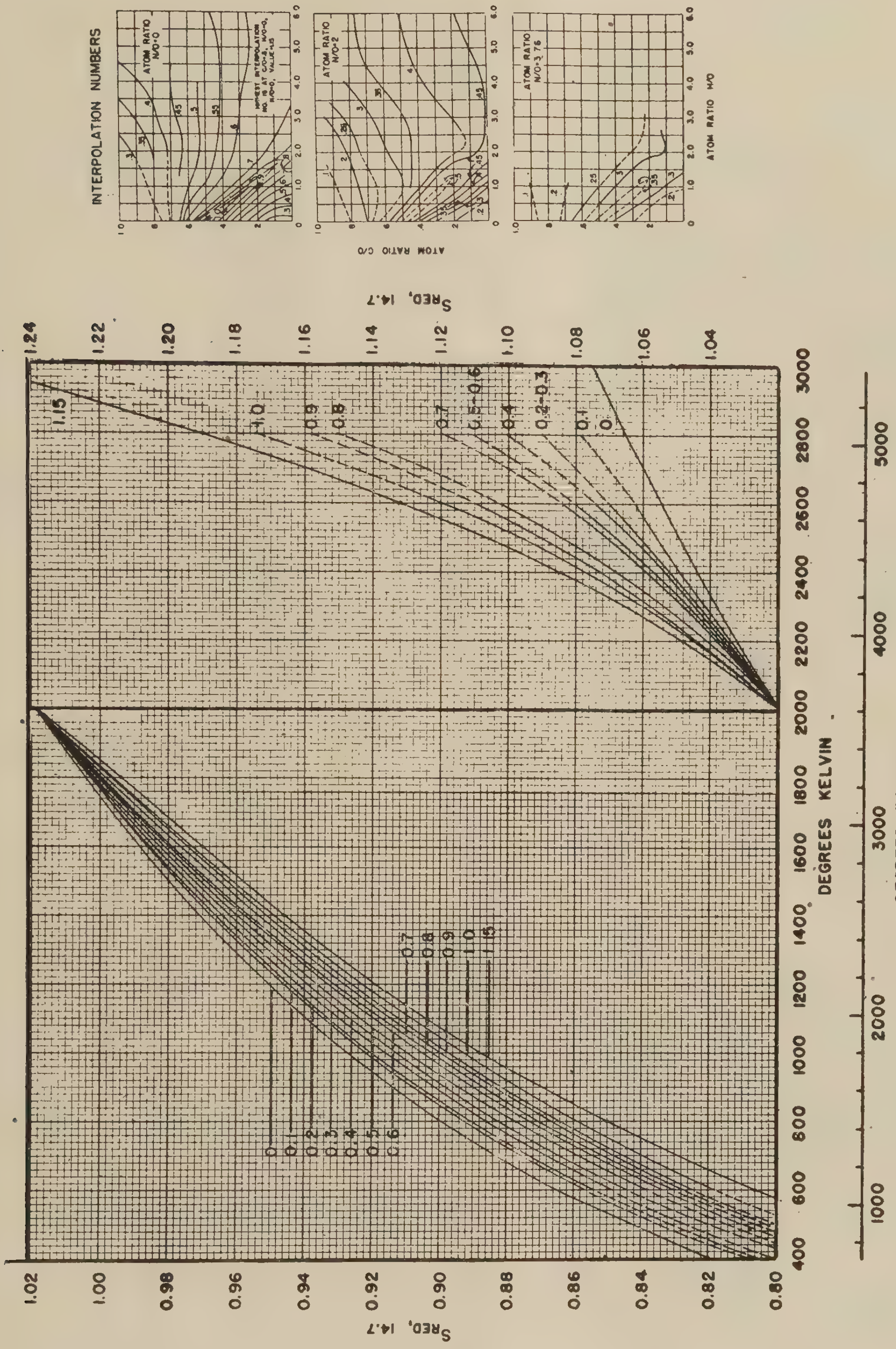

Fig. 4 Generalized Temperature-Entropy Relation for System C–H–O–N in Thermodynamic Equilibrium at 14.7 Psia

TABLE 2 ENTHALPIES OF SOME FUELS, OXIDANTS, AND DILUENTS

Chemical Specie	At 291°K Heat of Formation (Note a)	At 291°K Heat of Combustion (Note b)	ΔH from Substance at 300°K to Combustion Products at 0°K (See Footnote c) Btu/lb.mol		ΔH from Substance at 300°K to Combustion Products at 0°K (See Footnote c) Btu/lb.
CH_4 methane	18,240 (g)		343,060	liq.(at-161°C)	21,400
C_2H_2 acetylene (d)	-53,900 (g)		530,460	lio.(at-81.5°C)	20,390
C_2H_4 ethylene	-11,000 (g)		563,440	liq.(at-104°C)	20,100
C_6H_6 benzene		783,400	1,362,670		17,460
C_8H_{16} di-isobutylene		1,252,400	2,124,540		18,930
C_8H_{18} n-octane		1,305,000	2,203,400		19,290
C_9H_{20} nonane	+65,040		2,477,200		19,330
$C_{10}H_{18}$ decalin		1,502,500	2,559,600		18,530
CH_3OH methyl alcohol	57,450		281,340		8,784
C_2H_5OH ethyl alcohol	67,140		540,320		11,733
C_4H_3OCHO furfural		559,500	979,560		10,200
CH_3NH_2 methyl amine		256,100	425,770		13,710
$(CH_3)_2NH$ dimethyl amine	14,700		678,960		15,260
$(CH_3)_3N$ tri methyl amine		578,600	970,250		16,420
$C_2H_5NH_2$ ethyl amine	19,600		679,140		15,070
$(CH_2)_2(NH_2)_2$ ethylene diamine	14,500		743,420		12,370
$C_6H_5NH_2$ aniline		812,000	1,407,900		15,130
$C_6H_4(NH_2)(CH_3)$ o-toluidine		964,000	1,665,250		15,550
HCN hydrogen cyanide	-24,000		268,270		9,939
CH_3CN acetonitrile	-11,800		522,720		12,740
CH_3NC methyl isocyanide	-27,300		541,620		13,200
$C_{12}H_{12}N_2$ 1,2 diphenyl hydrazine		1,598,800	2,786,760		15,140
CH_3NO_2 nitromethane	27,600		285,660		4,680
$C_2H_5NO_2$ nitro ethane	33,000		552,240		7,360
$C_6H_2(CH_3)(NO_2)_3(s)$ trinitrotoluene		820,700(s)	1,466,460	(solid)	6,458
$C_3H_5(NO_3)_3$ tri nitro glycerine		432,400	760,680		3,350
H_2 hydrogen			102,400	liq.(at-255°C)	50,790
H_2O water	68,370		-14,600		-810
H_2O_2 hydrogen peroxide	45,200		28,840		848
O_2 oxygen			-1,818	lio.(at-183°C)	-57
O_3 ozone	-34,500 (g)		60,250	liq.(at-112°C)	1,255
N_2 nitrogen			-1,440	liq.(at-196°C)	-51
NH_3 ammonia	16,070		132,640		7,790
N_2H_4 hydrazine	-12,050		238,370		7,440
$N_2H_4.H_2O$ hydrazine hydrate	57,930		220,730		4,410
HNO_3 nitric acid	41,660		-14,270		-226
$NH_4NO_3(s)$ ammonium nitrate	87,130 (s)		65,450	(solid)	998
N_2O_4 nitrogen peroxide	6,140		180		1.96
Air (gaseous) (21.0% O_2-79.0% N_2)			3,750		130.4

(a) H_f = heat of formation in calories per gram mol at 291°K and 1 atm from the elements in their standard states (carbon as solid) to compound in question, in the liquid state unless specified gaseous or solid by (g) or (s).

(b) H_c = heat of combustion in calories per gram mol at 291°K and 1 atm from liquid fuel unless specified otherwise, to gaseous CO_2, N_2, and liquid H_2O.

(c) Heat evolved on cooling given compound in liquid form (unless specified otherwise) from 300°K (unless specified otherwise) to 0°K, plus heat released by burning with O_2 at 0°K to give CO_2, H_2O, (g), O_2, and N_2.

(d) Acetylene sublimes at -84°C and 1 atmosphere pressure and has a triple point at -81.5°C and 1.2 atmosphere pressure. To exist in the liquid state, therefore, C_2H_2 must be under a minimum pressure of 1.2 atmospheres.

to entropy and consequently is independent of partial pressure of the components.

Calculation of Propellant Performance in a Rocket Motor With Combustion Chamber at 300 Psia and Gases Exhausting to 14.7 Psia

The flame temperature at 300 psia is first determined as outlined, using Fig. 1. This temperature is then entered in Fig. 3 to give a reduced value for S_{red} at 300 psia. If reversible expansion through the nozzle may be assumed, $S_{\text{red},14.7} - S_{\text{red},300} = (\Delta_{14.7} - \Delta_{300})$. The value of the last term is obtained from Fig. 6. To obtain the exit temperature after expansion to 14.7 psia, the value of $S_{\text{red},14.7}$ is entered in Fig. 4. The exit temperature entered in Fig. 2 gives the value of H_{red} after expansion, and the change of enthalpy during expansion is obtained by difference.

The rocket exhaust velocity is obtained from the adiabatic energy balance

$$\frac{\Delta H}{W} = \frac{u^2}{2gJ}$$

u = velocity
W = mass of reactants
g = unit conversion factor
J = mechanical equivalent of heat

Then the specific impulse u/g, is given by

$$u/g = \sqrt{\frac{2J}{g} \cdot \frac{\Delta H}{W}}$$

It is to be noted that the foregoing method of calculation assumes that the chemical species involved remain in chemical equilibrium during expansion down to a temperature of 1600 deg K. Most rocket-performance calculations, on the other hand, assume that the gas composition is frozen during expansion, because of the simplification in the calculation that this assumption allows. The difference in the specific impulse, as calculated by the two methods, usually amounts only to a few per cent, and that only with high combustion-chamber temperatures.[5]

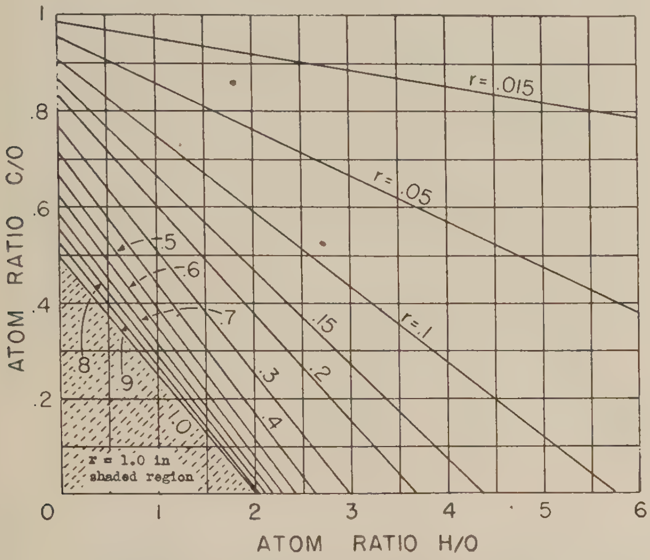

Fig. 5 Equilibrium Compostion of System Carbon–Hydrogen–Oxygen at 2000 Deg K, Considering Water-Gas Reaction Only
Values are given of ratio, r = mols CO_2/mols (CO_2 + CO); refer to text.)

Fundamental Thermodynamic Data

The basic data were taken or derived from a compilation by Hirschfelder, McClure, Curtiss, and Osborne (16). These data differ only slightly from those given by Lewis and von Elbe (17). Both compilations are based upon the same primary sources, with the exception that the values for water given by Hirschfelder, et al, contain a correction for stretching of the water molecule, evaluated after the publication of Lewis and von Elbe. The small differences in values for other chemical species are due to slightly different interpolations between the points given in the primary sources.

Example of Use of Generalized Data

The chemical engineer and mechanical engineer, in general, have different preferences in choice of base for combustion calculations; the chemical engineer prefers the molal basis, the mechanical, the pound. The charts of reduced functions of H and S obviously lend themselves equally well to the two bases. The following example will be calculated on a pound basis.

Calculate the adiabatic flame temperature and specific impulse of the system ethyl alcohol-liquid oxygen in the weight ratio of 1.5 lb of O_2 per 1 lb of C_2H_5OH. The mol ratio is 2.16 mol of O_2 per mol of C_2H_5OH.

The propellants will be pumped as liquids into an adiabatic combustion chamber operating at 300 psia. The products of reaction will be expanded reversibly and adiabatically to a pressure of 14.7 psia, chemical equilibrium being maintained during expansion.

The element ratios for this fuel-oxidant system and ratio are

$$\frac{C}{O} = 0.376, \quad \frac{H}{O} = 1.13, \quad \frac{N}{O} = 0$$

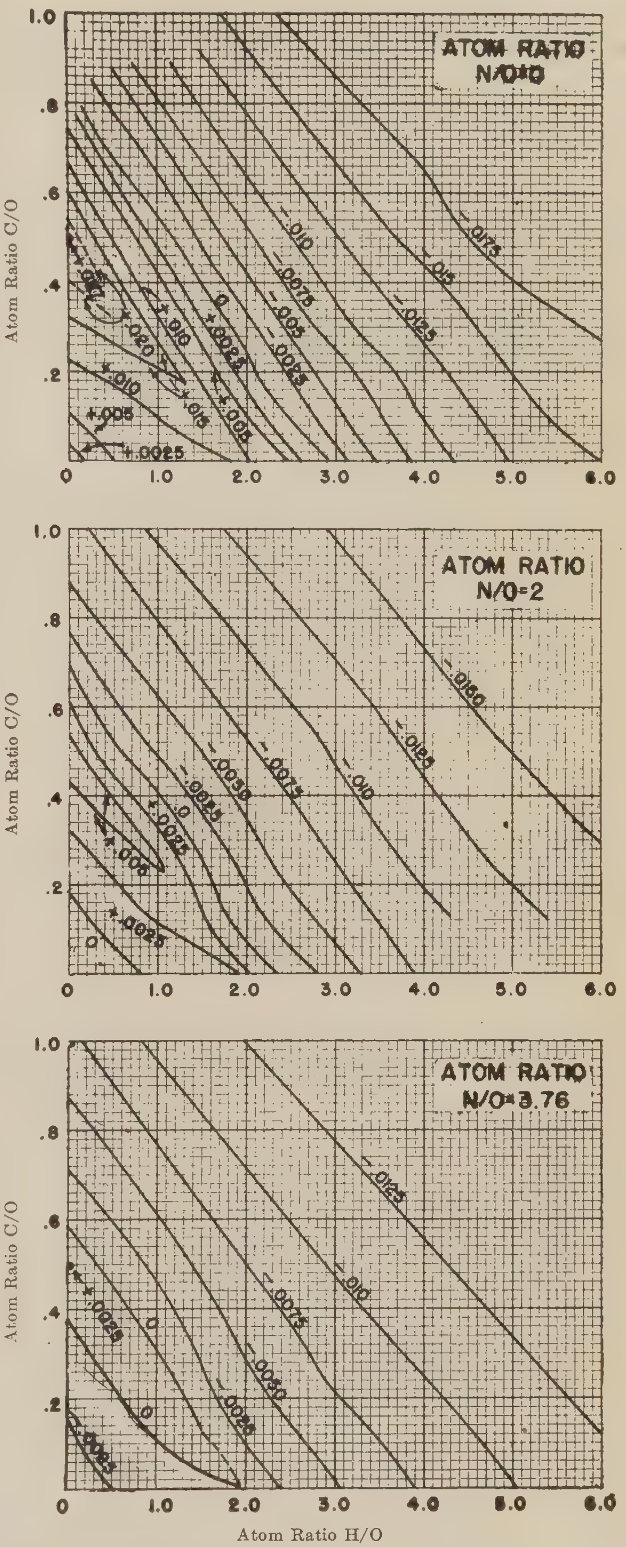

Fig. 6 Transformation Figures—Quantity ($\Delta_{14.7} - \Delta_{300}$) as a Function of Atom-Ratio Combination

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[5] In a number of calculations of the performance of commonly used propellants, the maximum difference obtained was about 6 per cent. The calculations assume the use of that nozzle in each case which produces the same desired discharge pressure. Calculations by the two methods but based upon the same physical nozzle will show performances varying by more or less than the figure cited, depending upon which process the nozzle was designed to fit.

Choose as a basis an amount of mixture containing one pound-atom of oxygen (16 pounds)

Fictitious Gas Composition:

The mixture contains

$$0.376\ \mathrm{C} \qquad 1.13\ \mathrm{H} \qquad 1.00\ \mathrm{O}$$

Since this corresponds to a fuel-rich mixture, one reads from Fig. 5

$$\frac{CO_2}{CO_2 + CO} = 0.46$$

$$\begin{aligned} CO_2 &= 0.46 \times 0.376 = 0.173 \\ CO &= 0.376 - 0.173 = 0.203 \\ H_2O &= \text{oxygen remaining} = 1.00 - 0.203 - 2 \times 0.173 = 0.479 \\ H_2 &= 1.13/2 - 0.451 = 0.114 \end{aligned}$$

On the basis of 1 lb of mixture

$$H_{f,0} = \frac{(0.203 \times 120{,}184 + 0.114 \times 102{,}794)}{2 \times 0.114 + 18 \times 0.451 + 28 \times 0.203 + 44 \times 0.113} = \frac{36{,}115}{21.64} = 1670$$

$$H_{f,2400} = \frac{(0.114 \times 135{,}218 + 0.451 \times 44{,}689 + 0.203 \times 154{,}620 + 0.173 \times 54{,}031)}{21.64}$$

$$= \frac{76{,}300}{21.64} = 3530$$

Enthalpy of Unburned Mixture

One pound of the fuel-oxidant mixture contains 0.60 lb of O_2 and 0.40 lb of C_2H_5OH. From Table 2 the total enthalpy of 1 lb of the mixture is 11,733 × 0.4 — 57 × 0.6 = 4659 Btu.

$$\frac{H - H_{f,0}}{H_{f,2400} - H_{f,0}} = \frac{4659 - 1670}{3530 - 1670} = 1.610$$

From Fig. 1, using an interpolation number of 0.4, the adiabatic flame temperature at 300 psia is 3140 deg K. This may be compared to a value of 3177 deg K reported by Wimpress and Sage (15).

From Fig. 3, using an interpolation number of 0.42, $S_{\mathrm{red},300} = 1.026$.

From Fig. 5, the quantity $\Delta_{14.7} - \Delta_{300} = +0.005$; hence $S_{\mathrm{red},14.7} = 1.026 + 0.005 = 1.031$.

From Fig. 4, using an interpolation number of 0.64, the temperature after expansion = 2130 deg K.

From Fig. 2, using an interpolation number of 0.42, $H_{\mathrm{red},14.7} = 0.884$.

$$\Delta H_{\mathrm{red}} = 1.610 - 0.884 = 0.726$$

$$\Delta H = 0.726 \times (H_{f,2400} - H_{f,0}) = 0.726 \times 1860$$

$$\text{Specific impulse} = \frac{2 \times 778}{32.2} \times 0.726 \times 1860$$

$$= 256 \text{ lb thrust per lb mass per sec}$$

This may be compared to a value of 243 reported by Wimpress and Sage (15), assuming frozen equilibrium after combustion.

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The Control of Structural Temperatures in Jet-Propelled Aircraft

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Laboratory tests were conducted for the purpose of obtaining empirical data on airplane structural cooling. This paper contains a description of the test equipment and the method of operation. Structural temperature measurements are reported for various insulating materials. Data, which indicate the effect of cooling air flow in combination with the insulating materials, are also presented. Some of the data are analyzed, and the magnitudes of effective conductances for use in preliminary design work are presented.

Nomenclature

The following nomenclature is used in the paper:

c = specific heat, Btu/(lb) (deg F)
C_b = apparent conductance of insulation, Btu/(hr) (sq ft) (deg F)
D_2 = average with length equivalent diameter of fuselage, ft
D_1 = diameter of tail pipe plus insulation, ft
F_{AE} = combination form and emissivity factor, dimensionless
G = mass velocity, lb/(hr) (sq ft)
h_C = forced-convection heat-transfer coefficient, Btu/(hr) (sq ft) (deg F)
h_F = total heat-transfer coefficient on outside fuselage surface, Btu/(hr) (sq ft) (deg F)
h_T = total heat-transfer coefficient on insulation surface, Btu/(hr) (sq ft) (deg F)
k = thermal conductivity, Btu/(hr) (sq ft) (deg F)/ft
q_{CA} = heat added to cooling air, Btu/sec
q_R = radiant heat transfer, Btu/sec
q_T = total heat transfer, Btu/sec
S_F = fuselage surface area, sq ft
S_R = tail-pipe radiating-surface area, sq ft
t_{CA} = average cooling-air temperature, deg F
t_F = average fuselage skin temperature, deg F
T_F = average fuselage skin temperature, deg R
t_{IN} = average insulation-surface temperature, deg F
T_{IN} = average insulation-surface temperature, deg R
t_O = room temperature, deg F
t_P = average tail-pipe temperature, deg F
μ = viscosity evaluated at average cooling-air temperature, lb/(hr) (ft)
μ_w = viscosity evaluated at inner-wall temperature, lb/(hr) (ft)

Introduction

The advent of the turbojet-engine installation in high-speed aircraft has presented serious problems in the control of structural temperatures which do not exist when reciprocating engines are employed.

The maximum allowable structural temperature for use in design is a disputed figure at the present time. Metallurgical tests conducted on aluminum alloys seem to indicate that yield strength and stress-rupture strength drop to low values at temperatures above 200 F. Basing an airplane structural design on these reduced strength values would result in a heavy structure; therefore the design temperature is taken as 200 F.

In order to achieve this allowable temperature, it is necessary to provide some method of limiting heat transfer from the hot turbine, tail pipe, and adjacent engine parts to the surrounding fuselage.

It can be seen readily that the means available for temperature control are: (*a*) an insulating blanket around the hottest parts of the jet engine; (*b*) cooling air flow passing between the jet-engine radiating surfaces and the adjacent structure; (*c*) some combination of cooling air flow and insulation; or (*d*) a close-fitting metal shroud around the engine and tail pipe with cooling air passing through the annular space between the shroud and engine. Various combinations of these four means have also been proposed.

The methods chosen for structural temperature control have an important effect on airplane performace. Utilization of an insulating blanket only would result in a heavy blanket. This is undesirable because the added weight of insulation would be detrimental to take-off performance which is often critical in jet-propelled aircraft. Controlling structural temperatures by means of high cooling air flows and not using an insulating blanket would also be undesirable for two reasons: (*a*) The cooling drag during high-speed flight would be prohibitive; and (*b*) the energy carried away from the exhaust gases by the cooling air would result in a lower energy content in the tail pipe which would in turn reduce the available jet thrust.

During the tests described in this paper, only the first three means of temperature control listed were investigated. The tests were primarily concerned with method (*c*). The question of insulation versus shroud protection is still highly controversial, and the authors do not intend to imply that the use of a shroud is undesirable, but rather that this method of temperature control was not investigated during the tests described.

From the considerations mentioned it should be evident that there is an optimum method of temperature control which would be satisfactory for both take-off and high-speed performance. If the combination insulation and cooling-air method of control is chosen, the problem finally becomes one of developing a satisfactory insulating material and determining the required cooling air flow to be used with it.

Of course the insulation to be used must have the lowest possible thermal conductivity per unit weight, and, in addition, should have the following characteristics: (*a*) Effectiveness at the elevated temperatures encountered on a jet engine; (*b*) adaptability to design and fabrication; (*c*) durability and ease of maintenance; (*d*) possession of handling qualities for ease of installation and shipment as a spare part; and (*e*) ease of removability to permit frequent inspection of the tail pipe.

A survey of available literature on the characteristics of high-temperature insulations revealed an almost complete lack of in-

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society.

formation on the subject. Also, a preliminary theoretical analysis indicated that the heat-transfer variables involved were so little known quantitatively that the mathematical approach could not be carried out to advantage without first obtaining experimental data.

For these reasons, it was decided to undertake an experimental program in an attempt to establish the magnitudes of the radiation and convection conductances involved. It was further decided to conduct the program on a full-scale test stand, in order to obtain sufficient data upon which to base an actual airplane design, and to eliminate uncertainties introduced by scale effects.

This paper concerns itself with a description of the test equipment and instrumentation developed. Also included are the methods of testing, and the results obtained for three types of insulating blankets. Some of these data are analyzed, and magnitudes of conductances for use in preliminary design studies are presented.

Description of Test Equipment

It was decided to construct only the tail pipe and surrounding fuselage rather than a complete engine installation, to facilitate ease of construction and operation of the test equipment. The full-scale section of fuselage constructed is typical of a high-speed jet-propelled fighter airplane. The test-fuselage frame dimensions, gage, and spacing are identical to an actual airplane.

The test tail pipe is also identical to the actual tail pipe in size, and is fabricated of stainless steel. The ends of the tail pipe are sealed and covered with asbestos filler blocks.

The forward end of the tail-pipe is supported by 4 cables, 90 deg apart, and bolted to the fuselage frame. The center of the tail pipe is supported by trunnions duplicating those in the actual airplane as closely as possible. Fig. 1 indicates the position of bulkheads in the test equipment, the location of the trunnion supports, and the test tail-pipe dimensions.

Two methods of heating the tail pipe were considered for the test equipment, namely, a furnace circulating hot gases, and electrical heating elements. Furnaces were rejected because of the difficulty in maintenance and handling. Also, the tail pipe had to be easily removable from the fuselage so that the insulation could be inspected at regular intervals. Electrical elements also offered more accurate selective control and ease of operation, and were therefore selected. The heating elements are located inside the tail pipe and consist of a "squirrel cage" of stainless-steel tubes supported within the tail pipe at a uniform distance of $^1/_2$ in. from the inner surface. Circumferential spacing is varied to compensate for nonuniform convection effects on the inside of the tail pipe. There are three groups of tubes for each half-length of the tail pipe, each group having independently controlled electrical input as a means of obtaining uniform tail-pipe temperature. Current is supplied to each of the six groups by the secondary of a 15-kva transformer. The cooling air flow is supplied by a centrifugal blower and controlled by a manually operated damper at the blower outlet.

Iron-constantan thermocouples are installed at the top, bottom, and each side of the inner flange at every frame. In addition, they are installed on each side of the fuselage skin at each frame, and on the trunnion tracks. Nine equally spaced chromel-alumel thermocouples are installed circumferentially at the center of each half-length of the tail pipe. On the insulation itself, four thermocouples are equally spaced along the length of the tail pipe and every 90 deg around it. Fig. 2 indicates the location of the thermocouples.

Cooling-air inlet temperature and temperature rise are measured with calibrated platinum resistance grids fore and aft of the test section. Details of these grids are contained in a report by M. A. Sulkin (1).[3] A bellmouth orifice, located at the blower inlet, is used to meter the cooling air flow.

The insulating blankets are installed only on the tail pipe and not on the discharge nozzle, because clearance problems in the actual airplane make insulating the nozzle impossible. In Fig. 1 the insulation extends from bulkhead 1 to bulkhead 10.

Description of Insulations Tested

Preliminary laboratory investigations indicated that several materials are relatively light in weight and possess sufficiently high thermal-resistance properties to warrant further consideration. Fig. 3, which is reproduced from a paper by D. Jelanik (2), indicates that Amosite has a low enough thermal conductivity over the range of temperatures shown, to warrant further consideration. The thermal conductivity alone, however, would only be helpful in selecting a material that would provide the required thermal resistance with minimum thickness. When weight is the most important consideration, the thermal resistance per unit weight is of primary importance. For this reason, Fig. 4, which is also reproduced from the paper (2) mentioned, was prepared. This figure indicates that leached Fiberglas is the most promising material. Amosite proved to be inferior to leached Fiberglas on a resistance per unit-weight basis. Based

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[3] Numbers in parentheses refer to the Bibliography at the end of the paper.

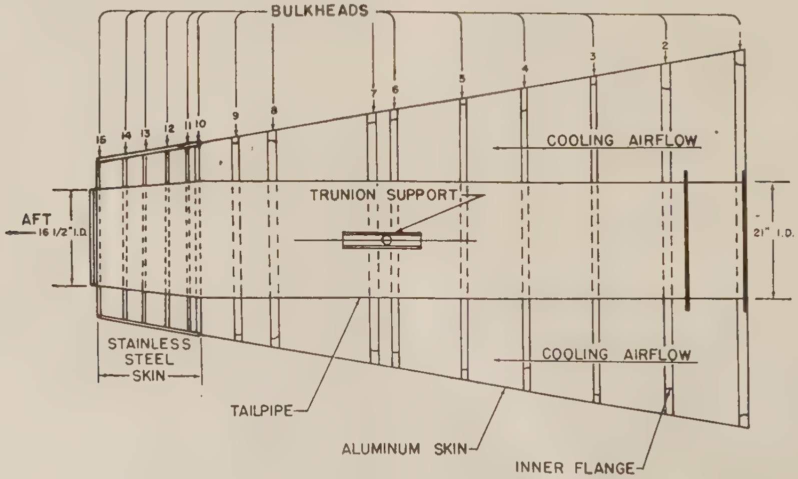

Fig. 1 Location of Bulkheads and Dimensions of Test Tail Pipe

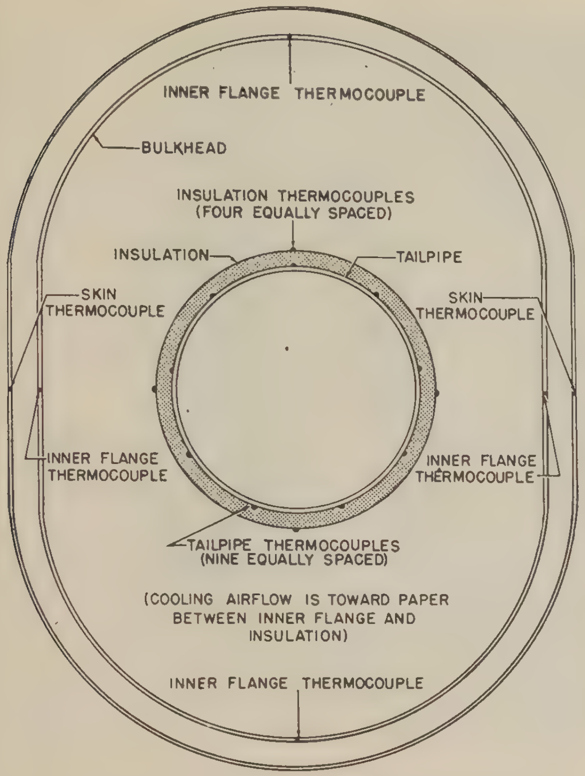
INNER FLANGE THERMOCOUPLE
BULKHEAD
INSULATION THERMOCOUPLES (FOUR EQUALLY SPACED)
INSULATION
TAILPIPE
SKIN THERMOCOUPLE
SKIN THERMOCOUPLE
INNER FLANGE THERMOCOUPLE
INNER FLANGE THERMOCOUPLE
TAILPIPE THERMOCOUPLES (NINE EQUALLY SPACED)
(COOLING AIRFLOW IS TOWARD PAPER BETWEEN INNER FLANGE AND INSULATION)
INNER FLANGE THERMOCOUPLE

Fig. 2 Location of Thermocouples at Typical Section

on the findings of this investigation, three insulating blankets were fabricated for testing. Two were fabricated of the most promising insulating materials, and the third is a type of radiation shielding which also showed promise in preliminary investigations. Starting with the hot side, the insulations are constructed as follows:

Amosite:

1 Knitted inconel wire mesh, 0.0045 in.
2 African long-fiber asbestos (density 9–10 lb per cu ft).
3 Glass cloth.

This blanket is quilted in 12-in. squares. The installed weight is 0.60 psf.

Radiation Shielding:

1 No. 40 stainless-steel wire mesh with $^1/_4$-in. corrugations.
2 Silver foil, 0.0005 in.
3 No. 40 stainless-steel wire mesh with $^1/_4$-in. corrugations.
4 Aluminum foil, 0.00045 in.
5 No. 40 stainless-steel wire mesh with $^1/_4$-in. corrugations.
6 Aluminum foil, 0.00045 in.
7 No. 26 wire mesh.

The installed weight is 0.89 psf. This insulation is not the lightest possible, since stainless-steel wire mesh was used only because aluminum wire mesh was not available. Also, lighter mesh than No. 40 could possibly be used. The installed weight with aluminum would be 0.35 psf.

Leached Fiberglas:

1 Knitted inconel wire mesh, 0.0045 in.
2 Silver foil, 0.004 in.
3 Leached fiberglas wool, $^1/_8$ in., 3 lb.
4 Aluminum foil, 0.00045 in.
5 Leached fiberglas wool, $^1/_8$ in., 3 lb.

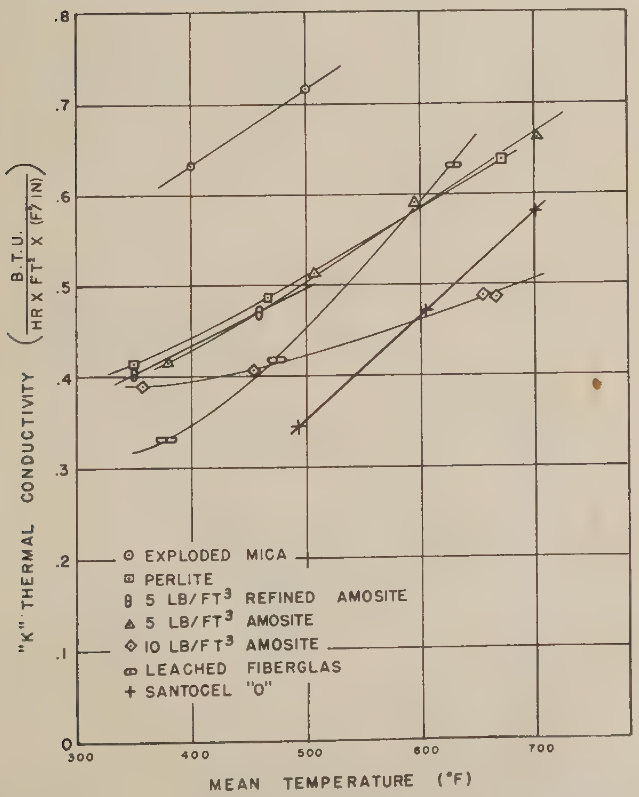

Fig. 3 Thermal Conductivity of Insulating Materials

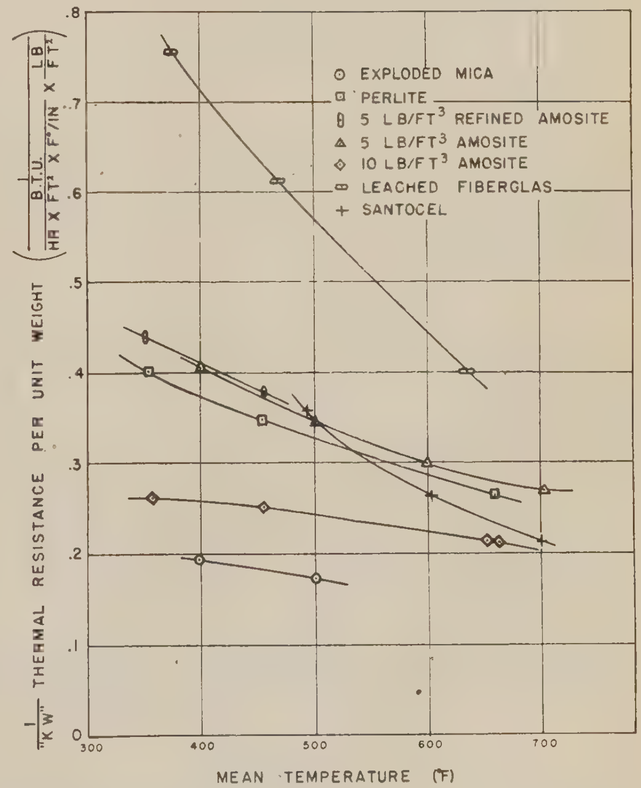

Fig. 4 Thermal Resistance per Unit Weight of Insulating Materials

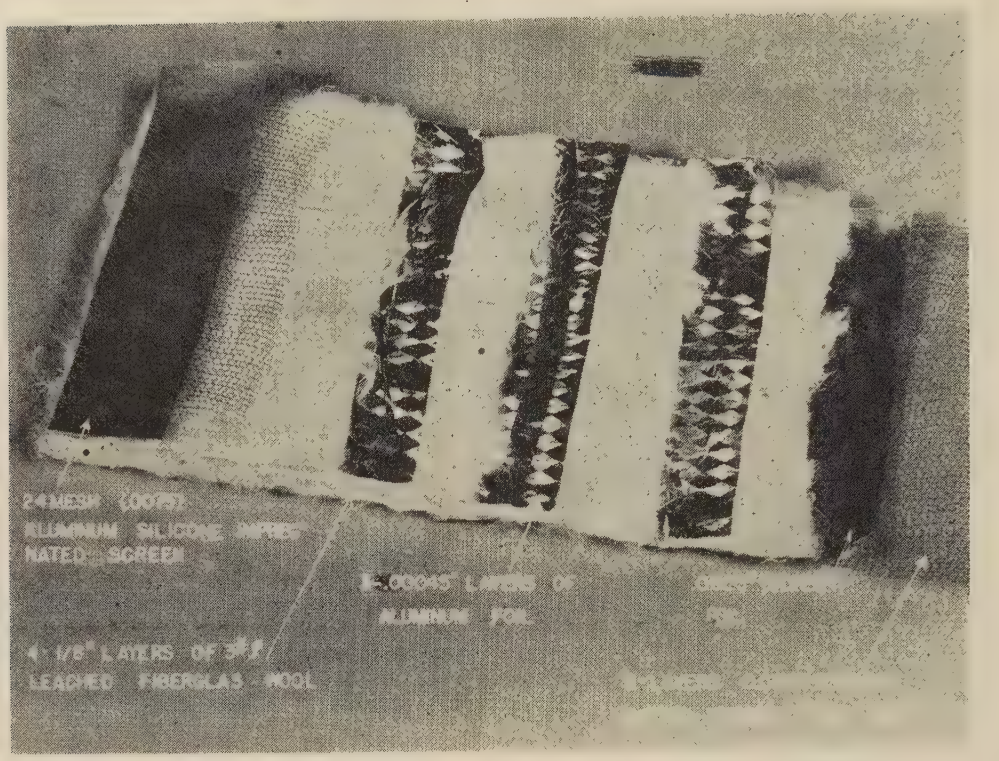

Fig. 5 Construction of Leached Fiberglas Blanket

6 Aluminum foil, 0.00045 in.
7 Leached fiberglas wool, 1/8 in., 3 lb.
8 Aluminum foil, 0.0045 in.
9 Leached fiberglas wool, 1/8 in., 3 lb.
10 Knitted inconel wire-mesh screen, 0.0045 in.
11 Aluminum-silicone-impregnated screen, 24 mesh.

The installed weight is 0.33 psf after heat-treating. On the basis of information obtained during the preliminary laboratory investigation, the leached fiberglas was heat-treated at 1600 F for 16 hr prior to fabrication. This heat-treatment preshrunk the blanket, which minimized the possibility of the blanket developing localized bare spots after installation. Fig. 5 is a view of this type insulation.

Experimental Procedure

The principal variable was the amount of cooling air flow passing through the annular space between the tail pipe and the fuselage. The procedure was the same for each of the three insulations tested.

The blower damper was adjusted to give the desired air flow prior to raising the tail pipe to operating temperature. If nonuniform pipe temperatures occurred, the individual heating elements were rotated circumferentially to compensate, and this process was repeated until a pipe temperature of 1200 F uniform within approximately 50 F was recorded. The test was repeated for air flows varying between zero and 4.0 lb per sec, and for a tail-pipe temperature of 1500 F. During each run, fuselage, insulation-surface, and cooling-air temperatures were recorded. The cooling air flow and electrical input were also recorded.

Discussion of Results

The results of the tests at various air flows with each insulation are plotted in a similar manner; skin temperatures and inner-flange temperatures are plotted against bulkhead number for various air flows. From inspection of these basic data, other curves were then derived.

Fig. 6 presents a typical curve of skin temperature versus bulkhead number for the leached fiberglas blanket at zero cooling air flow. Similar curves for the other two insulations indicated that both the trends and magnitudes of the temperature profiles were approximately the same. Plots of inner-flange temperature indicated that the profiles were similar to those of skin temperature; however, the inner-flange temperatures at any bulkhead

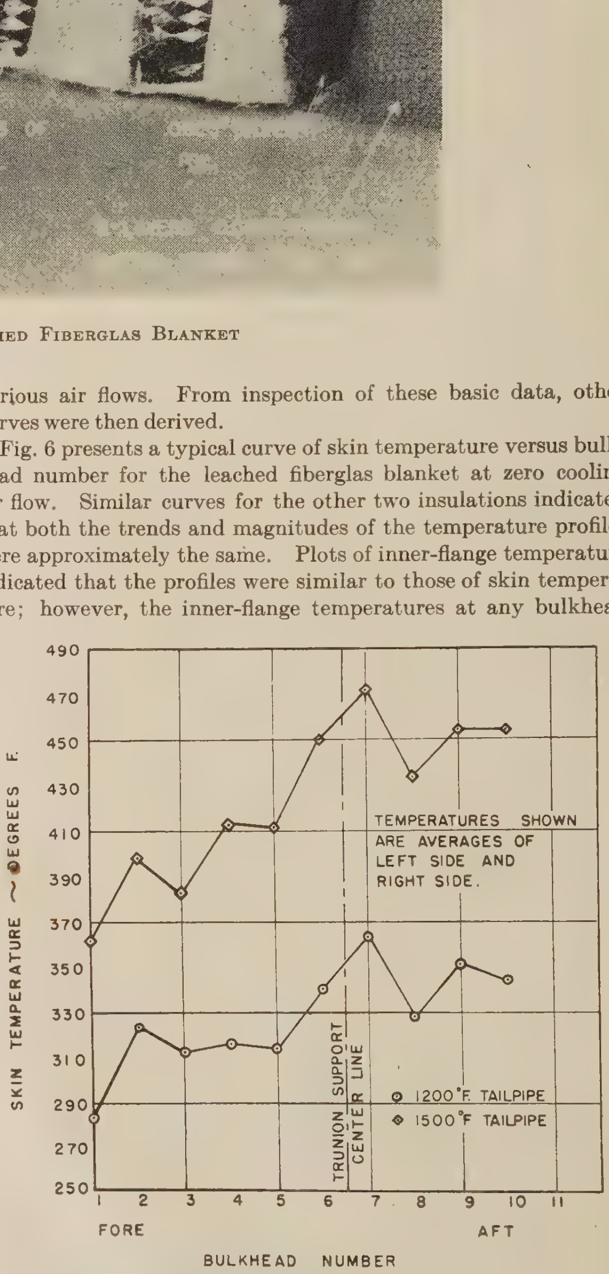

Fig. 6 Skin Temperature Versus Bulkhead Number for Leached Fiberglas Blanket

were 10 to 20 F higher than the corresponding skin temperature. The results for other air flows indicated that the general shape of the curve of temperature versus bulkhead number was the same for any air flow, and only the magnitude of the temperature decreased with increasing air flow. Due to the large volume of data gathered, only typical curves are included in this paper. The complete data are contained in recent report (3).

From an inspection of Fig. 6 it can be seen that the most critical cooling condition occurs at bulkhead 7, which is the aft trunnion support. This can possibly be explained by considering what occurs as the cooling air flows from fore to aft. The coefficient of heat transfer on the inside of the fuselage skin is increasing because of the increasing mass velocity, which would tend to cool the skin. Also, the cooling-air temperature is rising, which would tend to heat the skin. The two opposing trends result in a peak temperature, and this peak occurs at bulkhead 7 for all three insulations tested.

For bulkhead 7, the critical cooling location, skin temperature and inner-flange temperature were then plotted against cooling air flow, in order to determine the cooling-air flow required with each of the three insulations tested.

Fig. 7 indicates that the leached fiberglas required the lowest cooling air flow to maintain a 200 F skin temperature at bulkhead 7. This value is approximately 0.6 lb per sec. A similar curve for inner-flange temperature indicates that the leached fiberglas blanket requires approximately 0.75 lb per sec to maintain the inner flange at bulkhead 7 at 200 F. This curve may be found in reference (3), together with additional data for a 1500 F tail-pipe temperature.

One set of data were taken with zero air flow and no insulation, in order to determine what structural temperatures might result. It was found that maximum structure temperature occurred along the top of the fuselage at the bulkhead inner flanges. The results of this test indicate that the maximum structure temperature with no provision for cooling would be 640 F, and would occur at bulkheads 7 and 8. It should be pointed out that the thermocouples burned out before they were completely stabilized; however, the temperatures should still be indicative of the values that would exist if no provision were made for cooling.

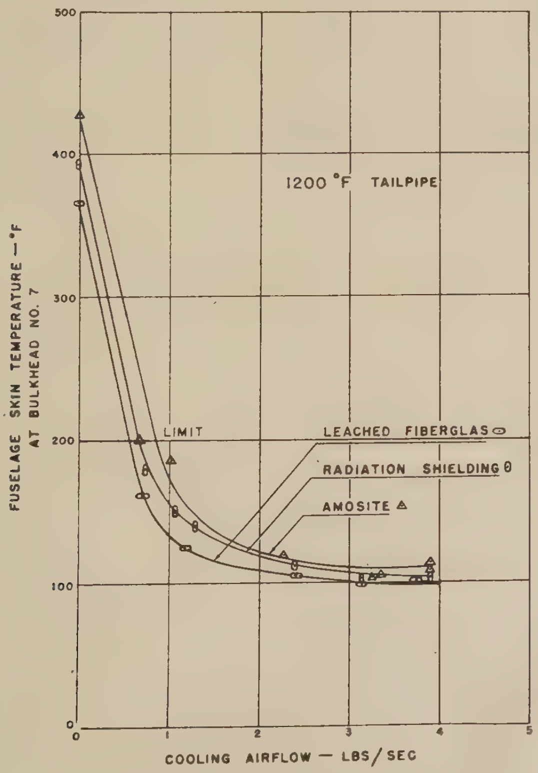

Fig. 7 Skin Temperatures Versus Cooling Air Flow at Bulkhead 7

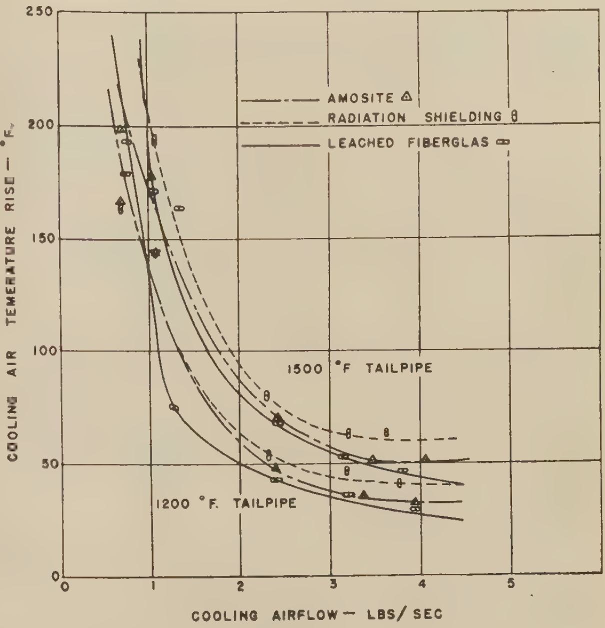

Fig. 8 Cooling-Air Temperature Rise Versus Cooling Air Flow

Fig. 8 presents the cooling air temperature rise as a function of cooling air flow for each of the three insulations tested. These data indicate that, at most values of cooling-air flow, the leached fiberglas blanket results in the lowest cooling-air temperature rise. This means that the least amount of heat is taken from the exhaust gases in the tail pipe, which would result in the highest available jet thrust.

Analysis of Results

A rigorous and complete analysis of the heat-transfer processes occurring was not attempted because of its complexity, and because the basic data obtained during the tests were sufficient upon which to base the airplane design. Some analysis was undertaken, however, in order to establish the validity of the results, and to determine the approximate magnitudes of the heat-transfer coefficients.

The heat transfer by convection from the insulation surface to the cooling air is composed possibly of two components, the rearward flow of air through the annular space between the fuselage skin and the insulation surface transfers heat by forced convection. Heat is also transferred by free convection owing to the displacement of the warmer and therefore lighter air up and around the hot tail pipe. Whether or not the two processes occur simultaneously is questionable, but it is felt by the authors that at the Reynolds numbers occurring during the tests, free convection from the hot insulation surface does not play an appreciable role.

A total heat-transfer coefficient for the air film on the insulation surface, based on the heat transferred by both forced convection and radiation was computed from

$$h_T = \frac{q_T \times 3600}{S_R\,(t_{IN} - t_{CA})} \quad\ldots\ldots\ldots\ldots\ldots\ldots [1]$$

It was decided to base all analyses on average temperature values rather than conducting a station-by-station investigation along the length of the tail pipe. The temperature t_{IN}, was evaluated as the average insulation-surface temperature, the temperature t_{CA} was evaluated as the average cooling-air temperature, and q_T was obtained from the electrical input. All data are contained in reference (3). The hydraulic diameter of the annular space was calculated from the known geometry by means of Equation [24] of reference (4), and the average value along the tail pipe was determined to be 1.7 ft. The average cross-sectional area was determined to be 6.7 sq ft from the essentially linear variation of cross-sectional area with length. The viscosity was evaluated at the average cooling-air temperature, and Reynolds number was then computed.

The total air-film conductance, computed from Equation [1], for each of the three insulations tested is presented as a function of Reynolds number in Fig. 9. The conductance is higher for the 1500 F tail-pipe temperature, principally because the higher insulation-surface temperature results in a higher rate of radiant heat transfer.

The values of conductances, presented in Fig. 9, are somewhat high, because a portion of the total heat transfer occurred through the uninsulated tail-pipe nozzle (bulkheads 10 to 15, Fig. 2). This portion of the total heat transfer would also tend to increase further the conductance for the 1500 F tail pipe over that obtained for the 1200 F tail-pipe. It is felt that the points which do not fall on the curves are scattered principally because of experimental error, especially where it was necessary to meter very low values of cooling air flow.

It should be pointed out that between a Reynolds number of zero, where free convection might occur, and the critical Reynolds number where turbulent flow begins, there could be a region where laminar flow occurs. It is felt that the accuracy of the data did not warrant this refinement, and therefore Fig. 9 was drawn as a smooth curve for all values of Reynolds number.

In an effort to compare the measured value of the total heat-transfer coefficient with theoretical values, forced-convection coefficients were calculated.[4]

The viscosity at the insulation surface was evaluated at the arithmetic average of the cooling-air temperature, and the insulation-surface temperature. All other physical properties were evaluated at the average cooling-air temperature. These con puted values of the forced-convection film coefficients are als shown in Fig. 9.

Since the data and the results previously discussed indicat that the leached Fiberglas is the most desirable insulating ma terial, the remaining analyses are concerned only with the on blanket.

In an effort to determine what percentage of the total hea transfer occurs by radiation from the insulation surface to th fuselage skin, the following analysis was completed: The radian heat transfer was calculated approximately.[5] The combinatio emissivity factor and form factor for two concentric cylinders one completely enclosed in the other, was assumed to approximate the geometrical relationship of the test equipment and wa calculated.[6]

The average value of this factor was determined, and was usec to calculate the average radiant heat transfer. The radiant hea transfer was expressed as a coefficient to be used with the insulation surface to cooling-air temperature difference by means o

$$h_R = \frac{q_R \times 3600}{S_R\ (t_{IN} - t_{CA})} = \frac{0.173\ F_{AE}\left[\left(\frac{T_{IN}}{100}\right)^4 - \left(\frac{T_F}{100}\right)^4\right]}{t_{IN} - t_{CA}} \quad [2]$$

The results of this analysis indicate that the radiant heat-transfer coefficient varies from 1 to 7 per cent of the total heat-transfer coefficient in all cases. The radiant heat transfer was found to decrease with increasing cooling air flow, which is probably caused by the cooling of the insulation surface.

It would be desirable to develop an empirical equation which could be used to predict the forced-convection heat-transfer coefficient that might exist under given conditions, since previous analysis has already shown that a standard equation from the literature is not satisfactory. This was done in the following manner: The computed radiant heat-transfer coefficients were subtracted from the total heat-transfer coefficients plotted in Fig. 9, which results in the value of the forced-convection film coefficients. These experimental values are shown in Fig. 10 as a function of Reynolds number.

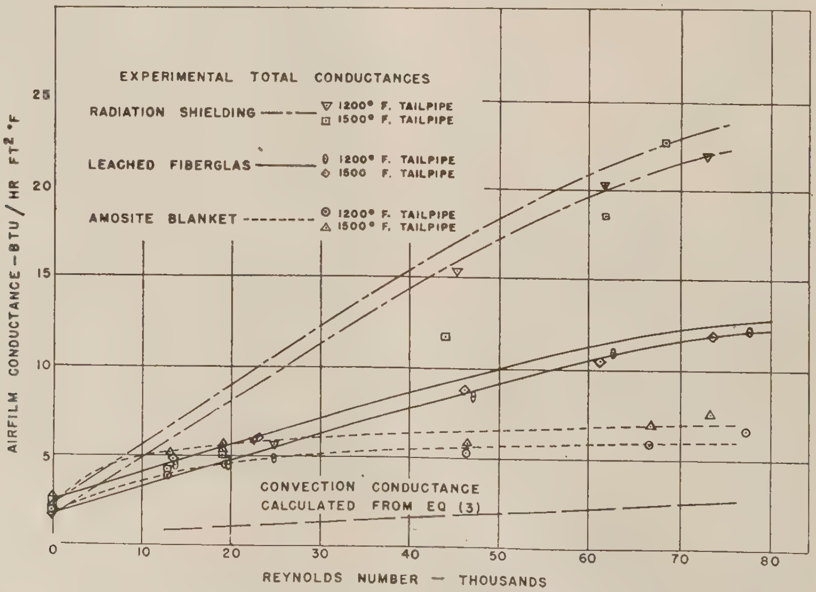

Fig. 9 Air-Film Conductance Versus Reynolds Number

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[4] Reference (5), Equation [1], p. 755.

[5] Reference (6), Equation [305], p. 175.

[6] Ibid., Equation [312], p. 180.

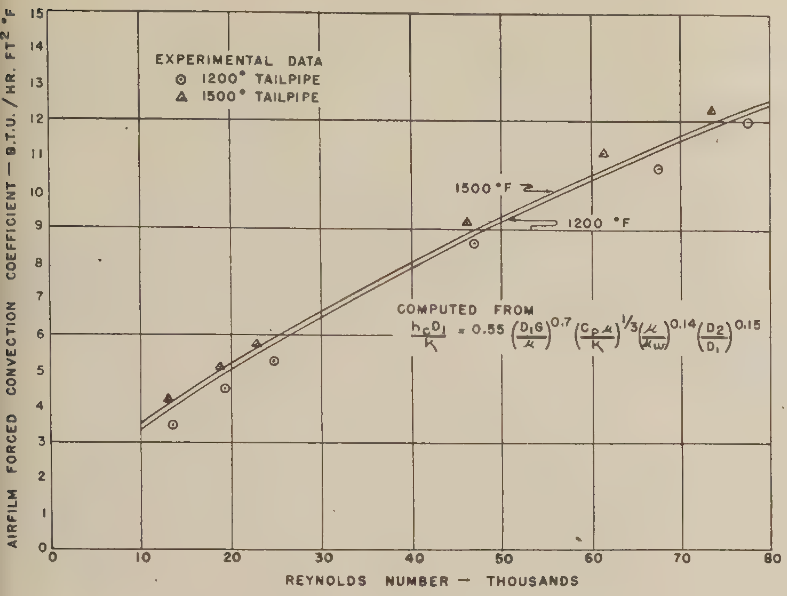

Fig. 10 Forced-Convection Coefficient Versus Reynolds Number for Leached Fiberglas Blanket

An equation similar to Equation [1][4] was then fitted to the experimental data. Assuming that all the discrepancy between the theoretical and experimental values is in the constant and in the Reynolds-number exponent, they were both empirically re-evaluated. The equation which fits both the 1500 F and 1200 F tail-pipe data most accurately is

$$\frac{h_C D_1}{k} = 0.55 \left(\frac{D_1 G}{\mu}\right)^{0.7} \left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{\mu}{\mu_w}\right)^{0.14} \left(\frac{D_2}{D_1}\right)^{0.15} \quad \ldots [3]$$

The values computed from this equation are also shown in Fig. 10. This equation differs from the experimental values by a maximum of 9 per cent.

It would also be desirable to determine the relative amounts of the total heat transfer that are carried away by the cooling air and are transferred from the outside surface of the fuselage by combined radiation and free convection. This was done in the following manner:

The total heat transfer was plotted against cooling air flow, and from the cooling-air temperature rise and cooling air flow, the amount of heat carried away by the cooling air was computed. The heat radiated and convected away from the outside of the fuselage was then obtained from the difference $q_T - q_{CA}$. The total fuselage film coefficient then was computed from

$$h_F = \frac{(q_T - q_{CA})\,3600}{S_F\,(t_F - t_O)} \quad \ldots\ldots\ldots\ldots [4]$$

In order to compare these experimental values of the film coefficient with values obtained theoretically, the total fuselage film coefficient was also computed.[7] The experimental results indicate that 2 to 7 per cent of the total heat input was lost from the outside surface of the fuselage at the higher values of cooling air flow. The heat balance at low values of cooling air flow was inaccurate because of the difficulties involved in metering cooling air flow. The average values of the experimental coefficients at any fuselage-skin temperature showed good agreement with the theoretical values; however, the individual points themselves showed a considerable scatter.

An analysis was also made to determine the apparent conductance of the leached fiberglas blanket as a function of the mean blanket temperature. The apparent blanket conductance was calculated from

$$C_b = \frac{q_T \times 3600}{S_R\,(t_P - t_{IN})} \quad \ldots\ldots\ldots\ldots [5]$$

This conductance is termed apparent because a portion of the total heat transfer is transferred through the uninsulated tail-pipe nozzle, and the conductance computed from Equation [5] therefore will be high.

The mean blanket temperature was taken as an average of the tail-pipe temperature and the outside insulation-surface temperature. The apparent conductance of the leached fiberglas blanket is presented as a function of mean blanket temperature in Fig. 11.

Fig. 11 shows a considerable amount of scatter in the data which could be due to either of two causes, namely, the effect of cooling air flow on the convective heat transfer through the uninsulated nozzle, or, the effect of cooling air flow on the blanket outside-surface thermocouple readings.

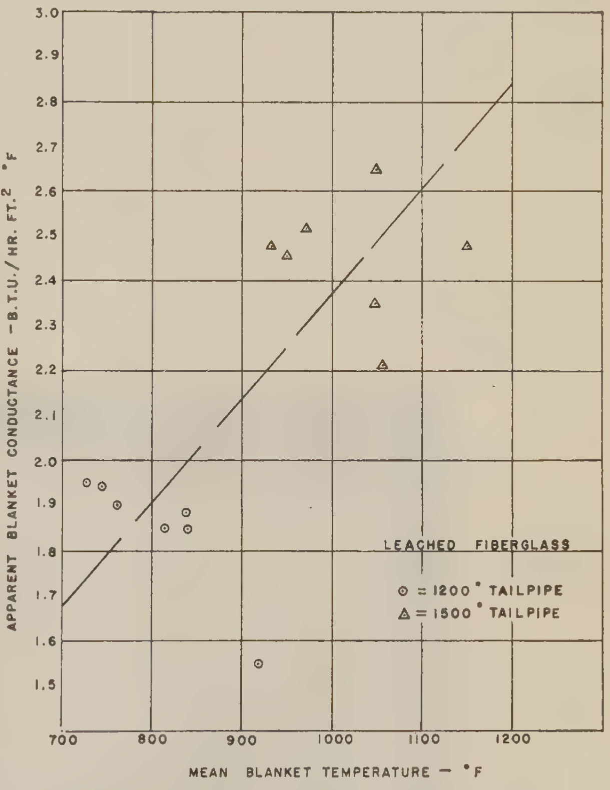

Fig. 11 Apparent Blanket Conductance Versus Mean Blanket Temperature for Leached Fiberglas Blanket

Conclusions

From the data and analyses previously discussed, it can be seen that the leached fiberglas type of insulation was found to be the most satisfactory. Its handling properties were excellent, and its insulative properties resulted in lower cooling air-flow requirements than either of the other two insulations tested.

It was found also that the fuselage frame supporting the aft trunnion fitting is the most critical in so far as cooling is concerned. The cooling-air flow requirements finally used for the airplane design were those required to keep the temperature at that frame to 200 F.

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[7] Reference (6), Equation [213], p. 93.

The analyses of the heat-transfer processes occuring indicated that of the total heat transfer through the insulation, 1 to 7 per cent was by radiation, and the remainder was by forced convection. Also, of the total heat input, 2 to 7 per cent was lost by free convection and radiation from the outside of the fuselage, and the remainder was carried away by the cooling air.

Some information on the handling properties of all three insulations was also gathered during the series of tests. It was found that the insulating properties of the Amosite blanket deteriorated upon installation because of the tendency for the filler to shift inside the blanket and leave void spots. The radiation shielding was found undesirable for three reasons: namely (*a*) it was difficult to handle; (*b*) it had to be constructed directly on the tail pipe rather than before installation; and (*c*) it was difficult to maintain the desired spacings between various layers of the shield.

Under actual service conditions, the leached fiberglas blanket previously described has a satisfactory life and appears to be quite durable. This life could possibly be increased by using thicker foils. No service experience has been gathered with the other two blankets.

The test described in this report was not intended to represent a summation of all the investigation necessary for proper airplane design, but rather as a starting point for future work. One topic that has not been touched upon is the cooling of small accessories in various parts of the airplane.

It is realized that more theoretical analyses could be completed, but the principal purpose of the test was to gather empirical data for a specific airplane and not to make a complete theoretical study of the heat-transfer processes occurring.

Tests on a ground-test stand of the entire airplane fuselage and flight tests of the airplane are being conducted, and more data on the structural temperatures existing under actual operating conditions should be available in the future. Fig. 12 shows the leached fiberglas blanket installed on the tail pipe of the jet engine used in the ground test stand.

Preliminary calculations of the inner-flange temperatures which might exist under typical flight conditions indicate that at low airplane speeds, owing to forced-convection heat transfer from the outside of the fuselage skin, the inner-flange temperatures would be from 20 to 40 F below the cooling-air temperature. At high airplane speeds, the adiabatic temperature-rise effect may cause the temperatures to be higher than under static conditions.

The results of this experimental program have served principally to design a satisfactory structural cooling system for jet-propelled aircraft, and also to establish preliminary design values for the parameters involved in the heat-transfer process which takes place in an airplane fuselage surrounding a jet-engine tail pipe.

ACKNOWLEDGMENTS

The authors express their appreciation to Mr. M. A. Sulkin of their company for the preliminary theoretical analyses made in order to determine the general nature of the tests, and for his continuous interest and assistance in the preparation of this paper; to the Engineering Research Laboratory staff for its preliminary testing of various insulating materials; and to the Experimental Department and Wind Tunnel personnel for constructing and assembling the test equipment.

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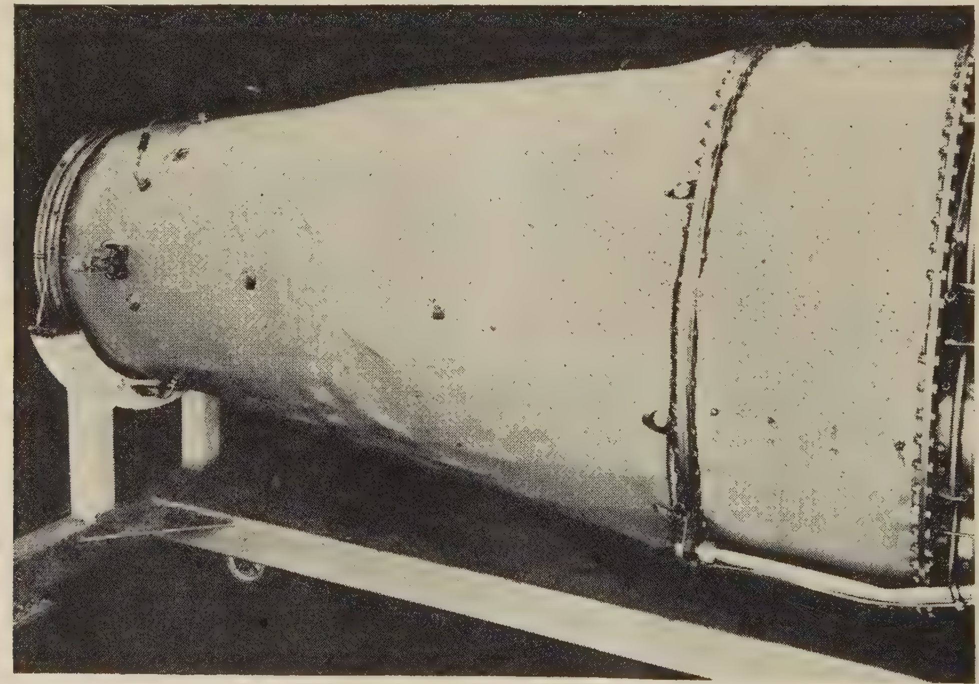

Fig. 12 Leached Fiberglas Blanket Installed on Actual Jet Engine

Temperature-Reduction Problems in Sugar-Beet Storage

By R. D. BARMINGTON,[1] FT. COLLINS, COLO.

Successful storage of sugar beets is dependent upon low storage temperatures. In parts of the United States where night temperatures are near the freezing point during the storage period, artificial ventilation during the night has been suggested as a means of removing heat from the beets. While this method has possibilities there has been a lack of knowledge and understanding regarding the large quantity of air required, and consequently the large blowers and ducts necessary. While the size of the structures would not be impractical, it is necessary to understand the magnitude of the problem before an attempt is made to design a commercial-size storage.

THE experimental work conducted in 1939 by Barr, Mervine, and Bice,[2] shows the amount of heat given off by sugar beets in storage at various temperatures. More recent work conducted by Stout and Fort[3] on large-scale storage piles has verified the earlier work and has indicated some new problems which arise when 10,000-ton storage piles are considered. Sugar losses in the storage pile vary from $^1/_4$ to 1 lb of sugar per ton per day, depending upon the temperature of the beet pile. Respiration of the living beet tissue consumes this sugar and gives off heat at the rate of 7098 Btu per lb of sugar. One pound of sugar per ton per day does not seem like a very large loss but when it is multiplied by 60,000 tons of beets stored in piles in one average-size factory district, it means that 30 tons of sugar are lost daily. It is the purpose of this paper to point out some of the problems involved in reducing the pile temperature to reduce sugar losses. Experiments conducted at this station and elsewhere have shown that a reduction in the pile temperature is the most effective way of reducing these losses.

Pile Temperatures Must Be Reduced Quickly

For best storage of sugar-beet roots the temperature must be reduced from approximately 50 F, the average temperature of the soil at harvest time in Colorado, to as near 32 F as possible without freezing. In addition to the sensible heat of the beets, it is necessary to remove the heat of respiration which in this temperature range is approximately proportional to the temperature of the beets. All of this heat must be removed as quickly as possible for best results. After the beet temperature has been reduced to the minimum desired it is only necessary to remove the heat of respiration which is 784 Btu per ton per day at 35 F.

It has been suggested that artificial ventilation of the sugar-beet pile, using night air which is usually 35 F or lower at this season of the year, might be a means of bringing the beet temperature down to reduce high sugar losses due to high respiration rates. Experimental results have shown that some benefits can be obtained in this way, but the quantity of air necessary is large and the cost of installing equipment of sufficient size might be too great to warrant the expenditure.

The Quantity of Air Can Be Calculated

The quantity of air required for any set of conditions can best be shown by deriving an expression for the heat transfer and using the values thus determined to apply to a specific problem.

Required to find the number of pounds of air necessary to reduce the temperature of 1 lb of beets from T_0 to T_1.

Since the specific heat of sugar beets has been found experimentally to be 0.86 Btu per lb per deg F, let Q_s = Btu of sensible heat in the beets and the amount to be removed = 0.86 Btu per lb per deg F

Q_r = Btu of heat generated per lb of beets and is a known function at the temperature T of the beets in Btu
C_p = specific heat of dry air at constant pressure = 0.241 Btu per lb per deg F
T = temperature of beets at any time
T_a = temperature of air (assumed constant entering the beets)
K = pounds of air flowing per hour per pound of beets
dT = change in temperature of beets in dt hr due to ventilation
dt = time during which K lb per hr of air are flowing

Assume the temperature of the air reaches the temperature of the beets during the time it is passing through the beet pile. Then for 1 lb of beets

Heat removed by air = $0.241\ (T - T_a)\ Kdt$

Heat removed from beets = $0.86\ (-dT) + Q_r$ (at temp T) dt

dT is negative because the temperature change of the beets is opposite to that of the air.

These two quantities must be equal

$$0.241\ (T - T_a)\ Kdt = 0.86\ (-dT) + Q_r\ (\text{at temp } T)\ dt$$

$$dt\ [0.241K\ (T - T_a) - Q_r\ (T)] = -0.86dT$$

$$\int_0^t dt = \int_{T_0}^{T} \frac{-0.86}{0.241\ K(T - T_a) - Q_r\ (T)}\ dT$$

$$t = \int_{T_0}^{T_1} \frac{-0.86}{0.241\ K(T - T_a) - Q_r\ (T)}\ dT$$

Kt = pounds of air required per pound of beets

$$Kt = K \int_{T_0}^{T_1} \frac{-0.86}{0.241\ K\ (T - T_a) - Q_r\ (T)}\ dT$$

Substitute X for Kt and assume $Q_r(T) = AT + B$

$$\text{Then } X = 0.86K \int_{T_0}^{T_1} \frac{dT}{0.241KT - 0.241\ KT_a - AT - B}$$

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[1] Associate Research Engineer, Colorado Agricultural Experiment Station.

[2] C. Guinn Barr, Colorado Agricultural Experiment Station; E. M. Mervine, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture; and R. A. Bice, California Agricultural Experiment Station. "A Preliminary Report on the Effect of Temperature and Beet Conditions on Respiration and Loss of Sugar From Beets in Storage," Proceedings, American Society of Sugar Beet Technologists, 1940.

[3] Myron A. Stout, Associate Physiologist, U. S. Department of Agriculture; C. A. Fort, Chemist, U. S. Department of Agriculture.

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NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society.

$$X = -0.86K \int_{T_0}^{T_1} \frac{dT}{(-0.241KT_a - B) - (-0.241K + A)\,T}$$

$$= \frac{-0.86K}{-D} \int_{T_0}^{T_1} \frac{-D\,dt}{C - DT}$$

Where

$$C = -0.241\,KT_a - B$$

and

$$D = -0.241\,K + A$$

$$X = \frac{0.86K}{D} \left[\log_e (C - DT)\right]_{T_0}^{T_1}$$

$$= \frac{0.86K}{D} \log_e \frac{(C - DT_1)}{(C - DT_0)}$$

or

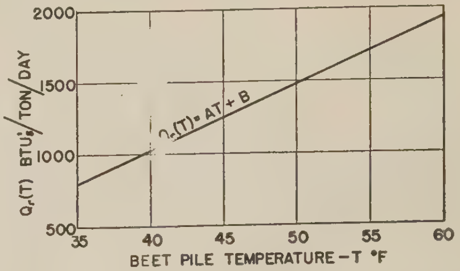
$$X = \frac{-0.86K}{D} \log_e \frac{(C - DT_0)}{(C - DT_1)}$$

It has been found experimentally by Stout and Fort that air at 27 F can be blown into the beet storage pile without damage to the beets if the temperature of the mass of the pile is above 32 F. Assuming the temperature of the beet pile is to be reduced from 50 F to 32 F using air at 27 F, and applying air at the rate of 0.02 lb of air per lb of beets per hr ($K = 0.02$), it would require 8.98 lb of air per lb of beets. In this case it would require 449 hr and a system having a capacity of 400,000 lb of dry air per hr for a 10,000-ton pile. To be of greatest value, the ventilating system should have capacity large enough to reduce the temperature in a much shorter time than just indicated. Since this is a logarithmic equation, less air is required per degree drop in beet-pile temperature at the beginning of the process than near the end. If the pile temperature is reduced only from 50 to 40 F, the amount of air required, other conditions remaining the same, is 2.92 lb of air per lb of beets. From the standpoint of reducing losses of sugar in the storage pile, even this 10 F temperature reduction is highly desirable since a change of temperature of 18 F in this range will approximately double or halve the rate of sugar loss from respiration.

Decomposition Begins at Higher Temperatures

Above approximately 65 F, decomposition of the living sugar-beet tissue begins, and a vicious cycle of increased temperature which causes increased respiration, that again causes increased temperature, results, and the beets rapidly heat and spoil. One of the values of forced ventilation is a kind of insurance against the forming of hot spots in the pile. These hot spots usually are caused by foreign matter, such as leaves and dirt, blocking the natural circulation of air in the pile. In the experimental work that has been done, a hot spot has never been found in the section of the pile being ventilated artificially. At a beet-pile temperature of 50 F, the amount of dry air at 27 F required to remove the heat of respiration would be 0.0052 lb of air per lb of beets per hr, since the heat of respiration at 50 F from Fig. 1, is 1390 Btu per ton per day. Using air at the same temperature of 27 F and beets at 60 F, the amount of air required to remove the heat of respiration is 0.0054 lb of air per lb of beets per hr.

At beet temperatures of 40 F and 95 F, the amount of air required is 0.0064 lb and 0.0161 lb, respectively. The changes in quantities of air are due to temperature differential between the air and beets and to the difference in respiration rates. The work of Barr, Mervine, and Bice[2] gives the heat of respiration of beets at 95 F, as 12,653 Btu per ton per day. This high value is due to the decomposition of the beet tissue which begins at about 65 F and increases rapidly as the temperature increases.



$A = 51.4$, $B = -1098$ } on basis of Btu per ton per day; $A = 0.0011$, $B = -0.023$ } on basis of Btu per lb per hr

Fig. 1 Effect of Temperature on the Heat Evolution of Sugar Beets

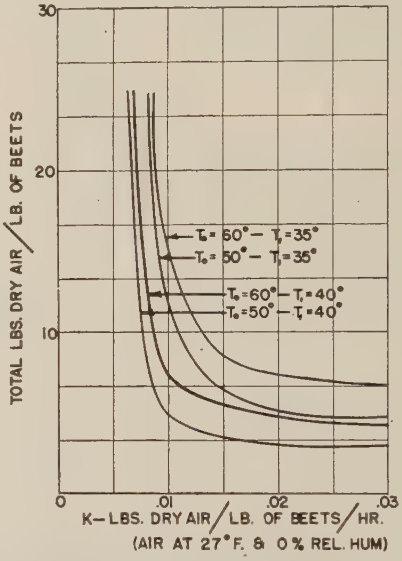


Fig. 2 Effect of Rate of Air Application on Total Air Required for Different Initial and Final Beet Pile Temperatures

Humidity and Evaporation Affect Rate of Cooling

There are two factors which tend to reduce the amount of air required for cooling the beet pile. The previous calculations are all based upon the use of dry air. Meteorological data at Fort Collins, Colo., shows the relative humidity during the sugar-beet storage period to be 70 per cent for a 48-year average of readings taken twice daily at 7:00 a.m. and 7:00 p.m. With air at 27 F and relative humidity of 70 per cent, each pound of dry air would carry in it 0.0020937 lb of water vapor. If no more water was added to the air as it passed through the beet pile, and if no evaporation of water takes place from the beets as the air temperature is raised from 27 F to 50 F, the heat taken up by the water vapor would be so small that it would be negligible.

The Btu of heat picked up by dry air is given by the equation $Q = W\,0.241\,(T_1 - T_2)$, and the heat absorbed by the water vapor is $Q = W\,0.46\,(T_1 - T_2)$. In changing from 27 F to 50 F, 1 lb of dry air will absorb 5.543 Btu, and the water vapor in 1 lb of air at 70 per cent relative humidity will absorb 0.02215 Btu of heat.

If the air enters the beet pile at 27 F and 70 per cent relative humidity and evaporates enough water while raising in temperature to 50 F so that it still has a relative humidity of 70 per cent,

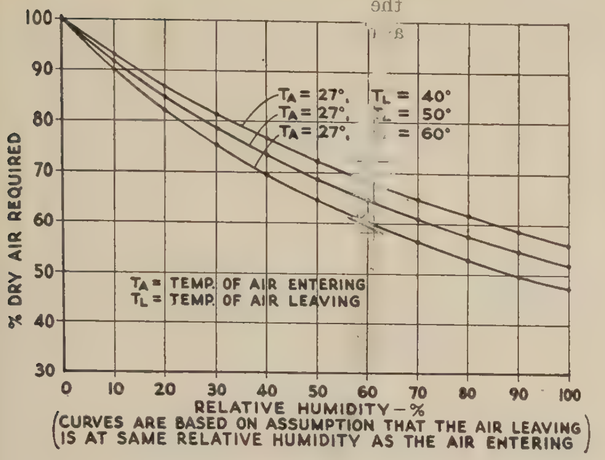


FIG. 3 EFFECT OF EVAPORATIVE COOLING ON TOTAL AIR REQUIRED

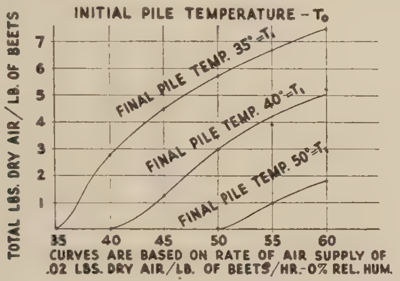


FIG. 4 EFFECT OF INITIAL AND FINAL PILE TEMPERATURE ON WEIGHT OF DRY AIR REQUIRED

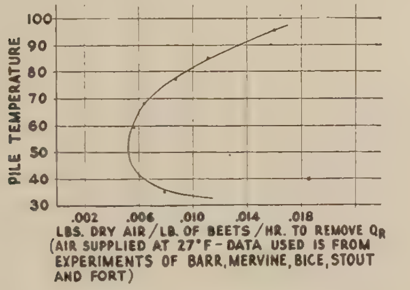


FIG. 5 AMOUNT OF DRY AIR REQUIRED TO REMOVE ONLY THE HEAT OF RESPIRATION

the air must also remove the latent heat of vaporization of the additional water necessary to maintain 70 per cent relative humidity. To maintain 70 per cent relative humidity while making the temperature rise, 1 lb of air must pick up 0.0029901 lb of water, making a total of 0.0050838 lb of water at 50 F. The latent heat of vaporization of 0.0029901 lb of water would be 2.9004 Btu, and the total heat removed from the beet pile by 1 lb of dry air plus the water vapor carried by the air entering the pile plus the water evaporated from the beets would be 8.46555 Btu. Under these conditions the removal of the same amount of heat from the pile would require approximately 65 per cent as much air as would be required if dry air alone was used.

The two factors, humidity and evaporation, are so closely related that they can hardly be separated. It can be seen that some cooling of the beet pile is accomplished at the expense of weight shrinkage which, if carried too far, is harmful from the standpoint of processing at the end of the storage period. There is not enough experimental information available to determine just what the conditions are in the beet storage pile when the heat transfer is taking place, but there is some evaporation of water which does tend to reduce the amount of cooling air required.

WEATHER CONDITIONS AFFECT THE DESIGN

In the Fort Collins area, the sugar-beet storage pile is from 14 to 18 ft high, 80 or more ft wide at the base, and 400 ft or more in length, and is piled in the open without side walls or roof protection of any kind. In this area there are occasional strong winds during the storage period which may occur either at night when temperatures are low or during the day when temperatures may be 60 to 70 F. If the winds occur at night, they are highly beneficial for cooling, but if they are warm the temperature of the pile may be raised several degrees. Greater control could be obtained by covering the sides of the pile but in this case all benefits of natural circulation at night would be lost and a ventilating system large enough to carry the full load would be necessary.

The ventilating fan should be designed to give large capacity at relatively low pressure, probably 1 in. of water or slightly less, since the voids between the beets are relatively large and, unless circulation is blocked by foreign material, the resistance to flow is low. Ducts should be large and adequate spaces should be allowed for the air to enter the beets.

MORE EXPERIMENTAL DATA NECESSARY

There seems to be a place for artificial ventilation in the storage of sugar beets. It will require further study and experimentation to determine whether or not it would be practical to build structures large enough to completely enclose for controlled ventilation all the beets now stored in the open.

In the Fort Collins factory district there are now 60,000 tons of beets piled in the open for a period of 40 to 60 days and, if the density is 40 lb per cu ft, this would require 3,000,000 cu ft of storage space. To cool these beets quickly for best storage conditions would require a ventilating system having a capacity of 4,800,000 lb of air per hr or 1,200,000 cu ft per min. Further studies and experiments with properly designed equipment will be necessary to determine whether or not a ventilating system would be economically sound. Large savings in sugar can be made if the temperature of the beet pile can be reduced quickly at the beginning of the storage period.

Condensation of Refrigerant Vapors—Apparatus and Film Coefficients for Freon-12

By R. E. WHITE,[1] YORK, PA.

In this paper is described an apparatus for the direct determination of condensing-vapor heat-transfer film coefficients in which precision measuring methods are employed. The conditions are closely controlled and can be made nearly ideal if so desired. Among the factors affecting condensation which may be studied in this apparatus are condensing temperature, film-temperature drop, noncondensable gas, liquid load on tubes, and condensing-surface condition. Included herein are data on the condensation of saturated Freon-12 under ideal conditions on a plain horizontal tube at various vapor temperatures and film-temperature drops.

Nomenclature

The following nomenclature is used in this paper:

A = area of heat-transfer surface, sq ft
D = outside diameter of tube, ft
g = acceleration due to gravity, ft/(hr) (hr)
h = film coefficient Btu/(hr) (sq ft) (deg F)
k = thermal conductivity, Btu/(hr) (sq ft) (deg F/(ft)
μ = viscosity of condensate, lb/(hr) (ft)
ρ = density, lb per cu ft
r = latent heat, Btu per lb
Δt = film-temperature drop, vapor temperature minus tube-surface temperature

Introduction

Heat-transfer film coefficients for condensing vapors have usually been determined indirectly from over-all coefficients, using the Wilson reciprocal plot. In some cases direct determinations have been made, but the measurement of the condensing-surface temperature is often inaccurate. As a result, accurate data on condensing film coefficients are not plentiful and particularly in the case of refrigerant vapors. It was hoped to obviate these difficulties by designing an apparatus utilizing a direct measure of condensing-surface temperature and other refinements, thus giving the condensing film coefficient directly. The factors affecting the condensation of vapors are manifold, and before effectual studies of complex cases of condensation can be made, each factor must be considered individually and dependable basic data obtained. Therefore, before undertaking an investigation of more complex cases, a complete study of the fundamental case of condensation of a saturated refrigerant vapor on a single horizontal tube under ideal conditions was deemed advisable.

Presented herein is a description of an apparatus designed primarily to give accurate heat-transfer data under closely controlled ideal conditions (the basis of the Nusselt derivation). Data showing the effect of film-temperature drop and condensing temperature on the condensation of Freon-12 are included to illustrate the success obtained with the apparatus. Incorporated in the design are provisions making the apparatus adaptable for studies on the effect of liquid load on the tubes, tube diameter, noncondensable gases, and condensing-surface condition on the condensing coefficient and for waterside and finned-surface studies.

Apparatus

The apparatus is basically similar to one previously described by the author (1).[2] The accuracy of the film coefficients obtained depends upon close control of the conditions and accurate measurement of several values, namely, vapor temperature, condensing-surface temperature, and quantity of heat transferred. Particular attention was given to these measurements. The methods and necessary precautions applied in this apparatus will be brought out more fully in the description. Other salient features include elimination of vapor velocity across or along the condensing surface, a nearly isothermal condensing surface, limited size, and provision for visual and photographic observation of the condensing surface.

A schematic diagram of the apparatus is shown in Fig. 1. The apparatus was designed to use $^5/_8$-in-OD tubes, 48 to 60 in. long as the condensing surface, since tubes of this size were being used in related experiments in the laboratory. Studies were expected to be made on chloro-fluoro-hydrocarbons and ammonia, and thus steel was a suitable material of construction. The use of copper, however, was minimized.

Condensing Surface

In order to check Nusselt's equation and to obtain truly comparable results over a period of time, a clean, noncorroding condensing surface of constant characteristics was needed. In view of the refrigerants to be tested and the foregoing requirements, highly polished nickel tubes were chosen as the condensing surface. Prior to use, these tubes were exposed to a Freon-12, water, and air mixture, alternating between the vapor phase and the liquid phase every 24 hr for 2 weeks. No visible change in the surface or change of weight occurred and thus it was assumed that either no corrosion occurred or it is at a very slow rate. These tubes were $^5/_8$ in. OD × 0.049 in. wall, 52 in. long. Two leads of no. 24 copper wire, silver-soldered in place, bracketed the central 36 in. of each tube. These served as potential leads in the tube-temperature-measuring means to be described later. Only one tube was installed in the apparatus for this first study. The surface exposed for heat transfer was 0.53 sq ft.

Boiler and Condenser

In order to obtain a minimum vapor velocity, in fact, only a velocity of approach to the condensing surface, the boiler and condenser were made an integral unit and the condensing surface was suspended in the vapor space. This also permitted the use of a small amount of the refrigerant in the test.

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-91.

[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

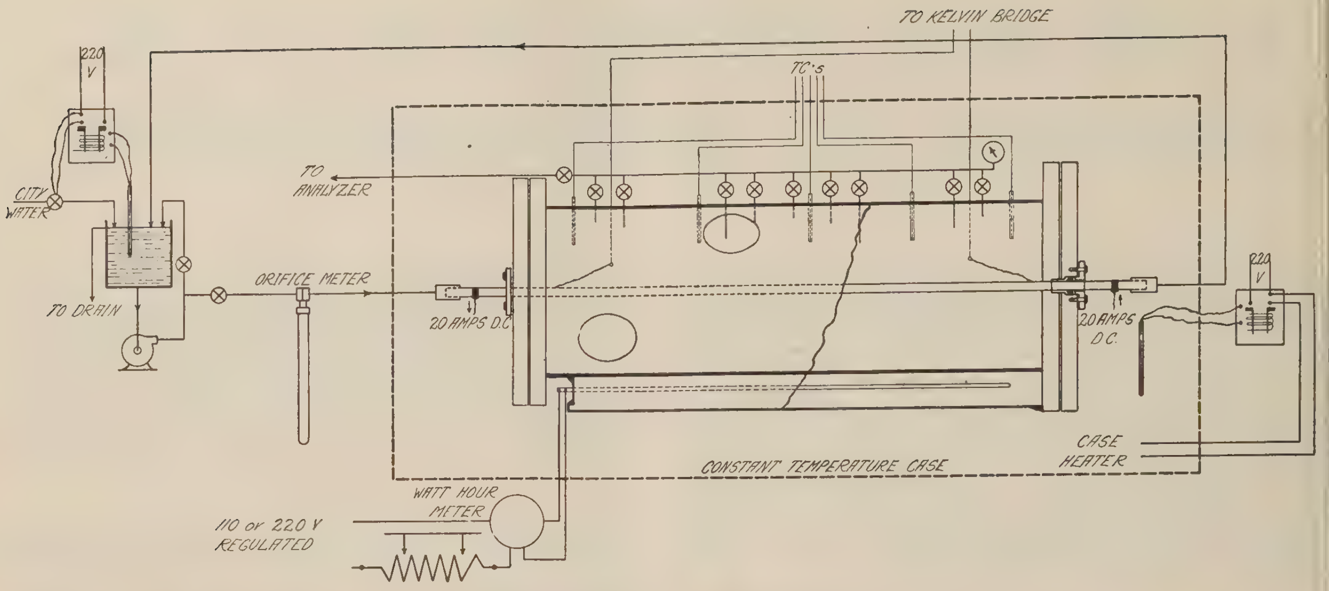

Fig. 1 Diagram of the Apparatus

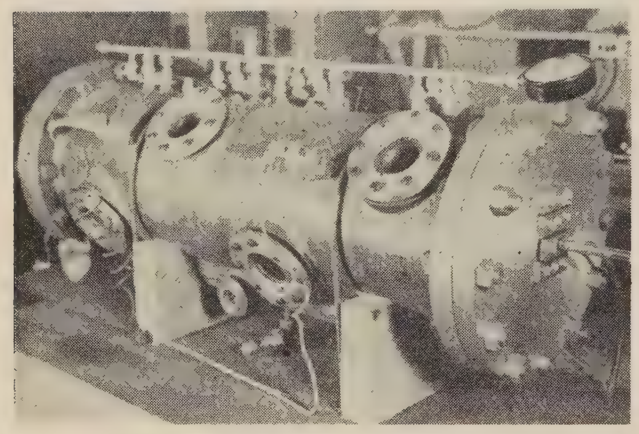

Fig. 2 Front View of Boiler-Condenser, Showing Sampling Valves, Bull's Eyes, and Tube Packing Glands Before Application of Insulation
(Condenser tube in place.)

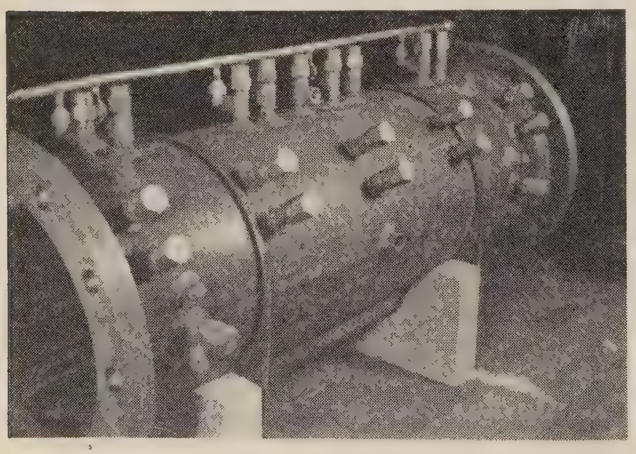

Fig. 3 Rear View of Boiler-Condenser, Showing Packing Glands for Thermocouples and Tube Potential Leads

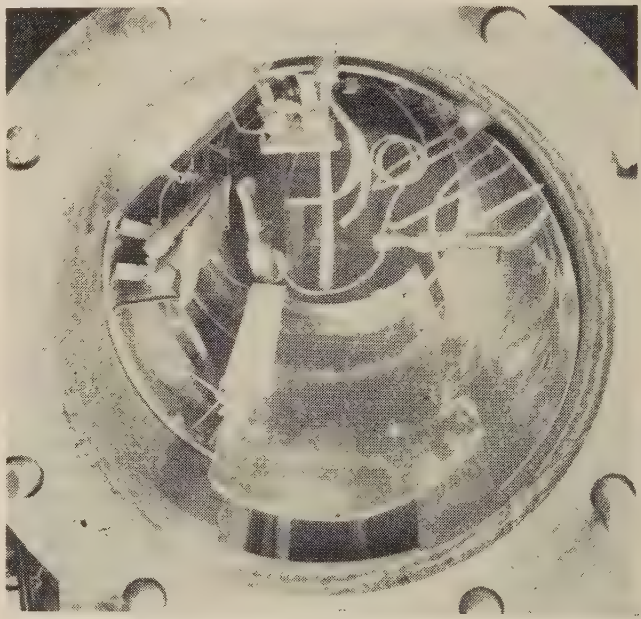

Fig. 4 Internal View of Boiler-Condenser, Showing Neon Lights, Sampling Tubes, and Thermocouples
(Calrod heater may be seen in boiler beneath baffle.)

The boiler and condenser are shown in Figs. 2, 3, and 4, at various stages of construction. The condenser shell is formed from a 40-in. length of 12-in. iron pipe with welded flanges on the ends. The boiler is formed from a 35-in. length of 5-in. iron pipe. An opening, 4 in. wide × 35 in. long, was cut longitudinally in each of these pipes and then, with the openings matched, the two pipes were welded together, thus forming a single unit. The boiler is closed on one end by the flange of the condenser and on the other by a $^3/_8$-in-thick welded head. This head carries two $^3/_4$-in-diam openings for the electric-heater leads.

The condenser is closed with identical $1^1/_4$-in-thick heads. Each head carries four individual packing glands, Fig. 2, for the tube or tubes that are to be placed in the vapor space. These glands are in perfect alignment and are spaced to give a $^3/_4$-in. bridge between $^5/_8$-in-OD tubes. Fiber sleeves and neoprene packing are used to insulate the tubes electrically from the heads at the packing glands.

Four 4-in. bull's eyes are spaced evenly along one side of the shell, two located on the upper 45-deg radius and two on the lower 30-deg radius.

Heat is supplied with a 3000-watt steel-sheathed Calrod heater in the form of a U, set into the boiler space with the leads passing through the openings of the boiler head. Closure to the head is made with packing glands. This heater has a 51-in. heating length and a power-output density of 38 watts per sq in. or 18,800 Btu per hr per sq ft. On the basis of a boiling coefficient of 400, the temperature of the heater sheath should not exceed the liquid temperature by more than 50 F. A low heater temperature is desirable to prevent decomposition of some materials.

A thin curved baffle, Fig. 4, is mounted 1 in. above the boiler opening and extends 1 in. beyond each side of the opening. This baffle directs the vapor to the perimeter of the shell and eliminates any direct impingement upon the tube.

Five 24-in-long tubular neon lights are mounted on the inside of the shell in such a way as to give suitable lighting to each tube when viewed through the bull's eyes. A 2-in. strip of opal glass is placed in front of each neon light to reduce glare and reflections on the condensing surface.

The condenser shell carries eight valved outlets spaced along the top of the shell for sampling the vapor. A $^3/_{16}$-in-OD tube extends inward, Fig. 4, from each of these outlets to various points within the vapor space. Twenty additional outlets are spaced about the shell and carry packing glands for withdrawal of thermocouple leads, tube potential leads, and neon-light leads. Several auxiliary openings are also provided for any future needs. After complete assembly, the boiler and vapor space was covered with 1 in. of insulating plaster.

Constant-Temperature Enclosure

By preventing heat flow through the walls of the boiler and condenser, all of the heat supplied by the electric heater has to pass through the heat-transfer surface. This heat quantity can then be derived accurately from the electrical input to the heater. The best method for preventing heat leakage to or from the boiler and vapor shell is to maintain the ambient temperature at the vapor temperature. This was accomplished by enclosing the apparatus in a temperature-controlled case. This case is constructed of a double layer of insulating board and has two doors for access to the apparatus and two windows aligned with the bull's eyes of the shell. Heat is supplied with eight, 100-watt light bulbs properly placed about the case. The temperature is controlled with a precision "Magna-Set" thermostat and an electronic relay in the power line to the light bulbs. For work below room temperatures, a direct expansion coil was placed in the case and used in conjunction with the lights. A bank of three blowers circulates the air in the case to maintain a uniform temperature.

Cooling-Water Circuit

In order to maintain an isothermal condensing surface, constant-temperature cooling water is pumped through the condenser tube at a rate sufficient to limit its rise to 0.25 F in passing through the condenser tube. Cooling water is pumped from a reservoir through a header, orifice meter, and the condenser tube and then returned to the reservoir. The inlet header carries four orifice meters, for use in later work. Flow through each orifice is controlled with a Hancock "Flo-Control" valve, and the excess pumped water is returned through a by-pass to the reservoir. The water temperature in the reservoir is maintained constant with a precision "Magna-Set" thermostat and an electronic relay which, through a solenoid valve, admits cold water as needed.

Electrical Heating Circuit

A wide range of controlled power input to the heater is provided to permit operation over a correspondingly wide range of film-temperature drops. The electrical circuit permits variation of power input from 160 watts to 3000 watts. Power is taken from a 220-volt controlled voltage line and, for the lower heat loads, this is transformed to 110 volts. The power input to the heater is adjusted by a Cenco-Forsythe water-cooled rheostat and measured on an integrating watt-hour meter.

Thermocouple System

The vapor temperature is measured with five copper-constantan thermocouples. Five $^3/_{16}$-in-OD steel tubes sealed at one end were inserted in the vapor space through packing glands. These tubes were bent in an L-shape so that at least 12 in. of each tube were exposed to the vapor, and the hot junction of each couple was then slipped into these tubes as far as possible. In this way, at least 12 in. of the leads of each hot junction were in the vapor space, thus eliminating any effect of heat conduction along the leads to or from the hot junctions. Three thermocouples were located in the constant-temperature enclosure to indicate its temperature. A common cold junction was used for all of the thermocouples. The constantan leads from the hot junctions and from the ice junction were converted to copper leads in a zone box before passing to a selective switchboard along with the hot-junction copper leads. The selective switchboard connected any hot junction with the ice junction and the emf-measuring means. The thermocouple emfs were measured on a Rubicon Type B potentiometer and Rubicon galvanometer. The sensitivity of these instruments is such that the emf's developed could be read with a precision equivalent to 0.02 F.

All of the thermocouples were calibrated prior to use while connected in the manner described. Calibrations were made at the ice point, the sodium-sulphate transition point, and the steam point, and the results were then plotted as deviations from Adams' values (2).

Tube-Wall Temperature Measurement

In determining film coefficients directly, an accurate measure of the tube-wall temperature has presented the most difficulty. Various methods of attaching or embedding thermocouples in the tube wall have been developed (1, 3, 4, 5, 6,) but such methods have their shortcomings (6). The electrical-resistance method described by Jeffrey (7) obviates these difficulties and yields an integrated and averaged tube-wall temperature without altering the tube-wall or surface conditions and does not necessitate a heavy tube wall. This method was used in this work.

The resistance of the central 36 in. of that part of the tube exposed to the vapor is measured with a Kelvin double bridge circuit by comparison with a standard resistance. The standard resistance used is an L. & N. Kelvin bridge and the bridge circuit is described in L. & N. bulletin, "Notes on the Kelvin Bridge." A direct current of 20 amp from a 6-volt storage battery flows through the tube and bridge circuit. The power is supplied through heavy leads connected to the ends of tube outside the condenser and the potential leads are withdrawn from the condenser through packing glands. To eliminate thermoelectric and parasitic currents, the resistance is measured with the current flowing through the tube in each direction, and the two readings averaged. The balance of the tube resistance and the bridge resistance is indicated on an L. & N. lamp and scale galvanometer.

This method requires a calibration of the tube prior to use to determine the temperature-resistance relationship. The nickel tube was calibrated by immersion in a vapor bath. The resistance of the central 36 in. of tube was determined at 10 F temperature intervals over the temperature range in which the tube would be used. The tube resistance was measured with a precision equivalent to 0.025 F. The temperature of the calibration bath was measured with the same thermocouples used later to measure the vapor temperature in the shell. In this way any basic error in the thermocouples would not be reflected in the measurement of the film-temperature drop. Periodic checks were made later between the tube and the thermocouples while in position in the condenser but no measurable shift in the relationship occurred.

Charging and Operation

Before charging, the boiler and condenser were evacuated to 20 microns pressure using an oil-sealed vacuum pump. This step insured a pure vapor without purging; its efficiency was established by subsequent analysis of the vapor which showed less than 0.001 per cent noncondensable present. Little difficulty was encountered in reaching this low pressure because of the limited size of the apparatus. Liquid refrigerant from an inverted drum was then charged into the boiler until the liquid level was about 1 in. above the Calrod heater.

In operating, the constant-temperature enclosure was brought to and maintained at the desired condensing temperature. The cooling-water thermostat was set to the temperature giving approximately the desired vapor-film temperature drop and the cooling water was then circulated through the tube at a predetermined rate sufficient to hold the water-temperature rise to less than 0.25 F. The power input to the Calrod heater was then adjusted to give the desired vapor temperature. A steady-state condition, as indicated by constancy of temperature readings, was usually established by transferring heat for about 1 hr. When equilibrium conditions were obtained, readings were recorded of the five vapor thermocouples, the three enclosure thermocouples, the tube-wall resistance, and the electrical heat input. A run was considered to be comprised of three sets of these readings taken over a $^1/_2$-hr period, in which each of the temperatures did not vary more than 0.1 F.

TABLE 1 SUMMARY OF RESULTS FOR CONDENSATION OF SATURATED FREON-12 ON A HORIZONTAL TUBE

Run no.	Average vapor temp, deg F	Average tube-wall temp, deg F	Tube-surface temp, deg F	Film temp. drop, deg F	Heat flux, Btu/-hr/ft²	Film coefficient, Btu/hr/ft²/deg F
1	119.52	99.08	99.41	20.11	5242	261
2	119.74	103.67	103.95	15.78	4555	289
3	120.00	105.55	105.81	14.19	4038	287
4	119.89	109.40	109.60	10.39	3129	301
5	119.97	112.03	112.19	7.76	2494	321
6	119.82	114.95	115.06	4.76	1742	366
7	119.81	116.41	116.50	3.31	1362	412
8	119.56	116.92	116.99	2.57	1105	430
9	119.78	107.61	109.84	11.94	3539	296
10	119.86	103.30	103.58	16.28	4431	272
11	119.81	97.45	97.80	22.11	5543	251
12	90.23	78.21	78.44	11.79	3639	309
13	89.98	76.73	76.98	13.00	3991	307
14	89.99	73.52	73.82	16.17	4780	296
15	90.08	69.84	70.20	19.88	5603	282
16	89.91	77.16	77.41	12.50	3881	311
17	90.13	80.05	80.26	9.87	3275	332
18	90.09	85.78	85.89	4.20	1730	412
19	89.85	87.02	87.10	2.75	1276	464
20	89.98	86.63	86.73	3.26	1456	447
21	90.14	87.23	87.32	2.84	1326	470
22	90.07	84.01	84.16	5.91	2282	386
23	90.08	76.76	77.01	13.07	3925	300
24	70.10	52.82	53.14	16.96	5070	299
25	69.78	54.61	54.90	14.88	4552	306
26	69.97	57.49	57.74	12.23	3930	321
27	70.15	59.69	59.92	10.23	3502	342
28	70.26	62.31	62.50	7.75	2875	371
29	69.63	64.43	64.56	5.07	2051	405
30	69.74	60.85	66.94	2.80	1334	477
31	70.08	66.87	66.96	3.12	1429	458
32	70.15	59.13	59.37	10.78	3645	339
33	70.26	57.21	57.48	12.78	4165	326
34	70.21	52.55	52.88	17.33	5190	299
35	50.46	38.24	38.50	11.93	4050	339
36	50.27	40.75	40.97	9.30	3360	362
37	50.33	42.71	42.89	7.44	2800	376
38	50.23	44.22	44.37	5.86	2305	393
39	49.93	44.16	44.30	5.63	2260	401
40	50.10	41.37	41.57	8.50	3117	367
41	50.10	38.83	39.07	11.03	3845	349
42	50.10	37.55	37.81	12.29	4111	334
43	50.09	44.96	45.09	5.00	1946	389
44	50.24	45.53	45.66	4.59	1936	422
45	50.00	46.36	46.46	3.54	1591	449

Results

A series of runs were made at each of four condensing temperatures, namely, 120 F, 90 F, 70 F, and 50 F. Each series consisted of ten to fifteen runs in which the condensing-film temperature drop was varied from 3 F to 20 F.

The five vapor thermocouple readings were converted to temperatures using the individual calibration for each couple and then averaged. Likewise, the average tube-wall temperature was obtained from the tube-wall resistance-temperature calibration. The additional 2 in. of condenser tube exposed to the vapor on either end of the central 36 in. does not affect the average tube-wall-temperature value since both sections conduct practically the same amount of heat, and end losses are eliminated by maintaining ambient temperature at the vapor temperature.

The heat-input reading (from the integrating watt-hour meter) was converted to Btu per hr (q), and this value, in turn, gave the heat flux q/A, when divided by the condensing-surface area (A = 0.53 sq ft). From the heat flux and the conductivity of the tube material, the temperature gradient across the tube wall is calculated. The average tube-wall temperature plus one half the gradient gives the tube-surface temperature. The film coefficient

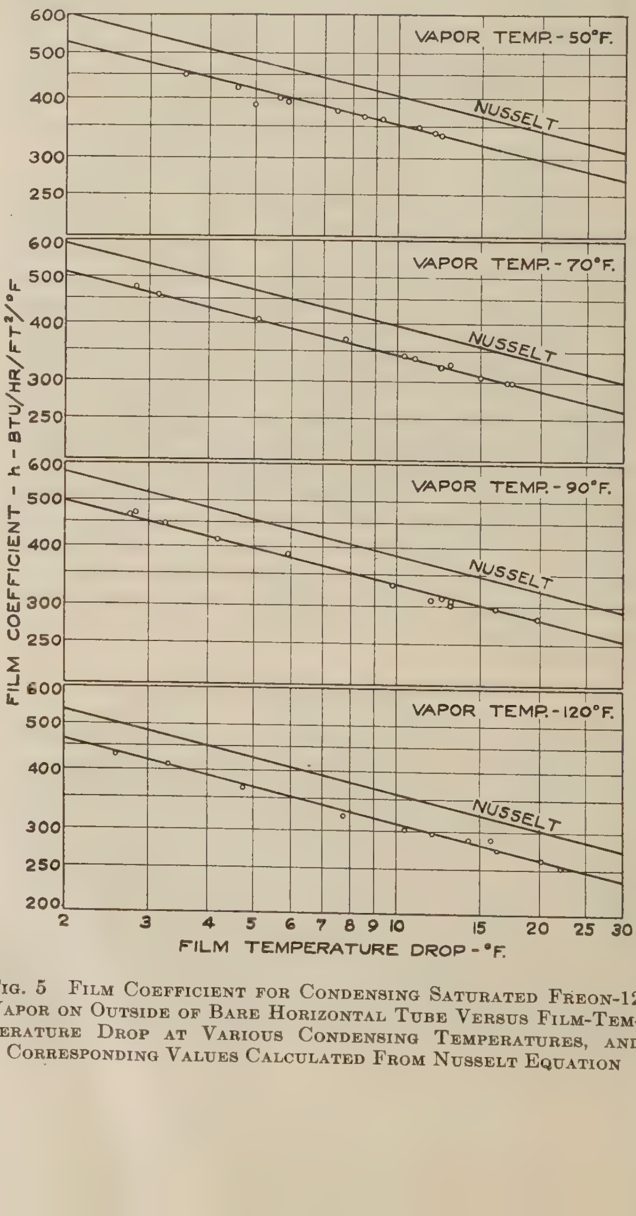

Fig. 5 Film Coefficient for Condensing Saturated Freon-12 Vapor on Outside of Bare Horizontal Tube Versus Film-Temperature Drop at Various Condensing Temperatures, and Corresponding Values Calculated From Nusselt Equation

h, is then obtained by dividing q/A by t, the difference between tube-surface temperature and the average vapor temperature. These calculated results are given in Table 1.

Correlation of Data

The results in Table 1 were plotted on logarithmic scales in Fig. 5, as film coefficient h, against film-temperature drop Δt, for each condensing temperature.

A straight line of —0.25 slope was drawn through the data points for each condensing temperature. In drawing these lines, an attempt was made to weigh and average the data, giving more weight to the points representing higher values of Δt. The use of the theoretical slope of Nusselt's equation appears well justified in this case since over 90 per cent of the data points fall within 2 per cent of their respective lines.

In Fig. 6 the plots of experimental data in Fig. 5 have been combined to point up the consistency between series of runs, and also to bring out the effect of condensing temperature on the coefficient.

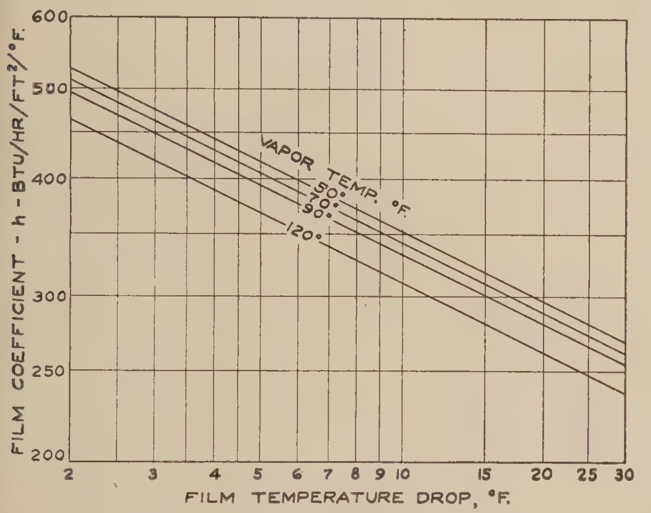

Fig. 6 Plot of Coefficient Versus Film-Temperature Drop Showing Effect of Condensing Temperature on Coefficient

Values of film coefficient h, at the various condensing temperatures were calculated from the physical properties of Freon-12 using the Nusselt equation

$$h = 0.725 \sqrt[4]{\frac{k^3\rho^2gr}{D\mu\,\Delta t}} \quad \text{[1]}$$

Lines representing these theoretical values for each condensing temperature were then drawn on Fig. 5 for comparison with the experimental results. The values for viscosity and thermal conductivity used in this correlation were based upon newly determined data not yet released for publication. These data, believed to be more accurate than previously published data (8), differed from published values by 10 to 20 per cent in the case of viscosity, and 5 to 10 per cent in the case of thermal conductivity.

The experimental data fall 13 per cent below the Nusselt lines at all condensing temperatures, thus indicating a simple correlation in the form of a modified Nusselt equation. This new equation is

$$h = 0.63 \sqrt[4]{\frac{k^3\rho^2gr}{D\mu\,\Delta t}} \quad \text{[2]}$$

and represents the average experimental data within 1 per cent.

When using published data for all of the physical properties, this simple agreement did not exist. The Nusselt lines maintained a—0.25 slope of course but their spacing differed considerably from that of the experimental lines.

It is interesting to note that the results of Young and Wohlenberg (9) yield an average constant in the Nusselt equation of 0.655. Katz, et al (10) gave a value of h, based upon over-all coefficients, that is, about 12 per cent below the Nusselt value calculated herein.

Conclusions

An apparatus has been constructed for the direct determination of condensing-film coefficients of heat transfer on horizontal tubes under closely controlled conditions. A number of novel features have been combined to increase the precision of the measurements and the accuracy of the results. The data indicate the success attained along these lines. Experimental data obtained under conditions as nearly ideal as possible are 13 per cent below the low values predicted by the Nusselt equation for condensation of Freon-12 at elevated pressures.

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Prediction of Pressure Drop During Forced-Circulation Boiling of Water

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A tentative method for the rapid calculation of the pressure drop during forced-circulation boiling of water is presented. The method is based upon the application of pressure-drop data, obtained during the isothermal flow of air and various liquids, to the evaluation of local pressure gradients during forced-circulation boiling. Curves are developed by means of which the pressure drop during boiling can be estimated quickly once the exit quality, the boiling pressure, and the pressure drop for 100 per cent liquid are known. The proposed method is definitely an extrapolation of existing data and, as such, requires further experimental verification.

Nomenclature

The following nomenclature is used in the paper:

A_y = heat-transfer area = πDy, sq ft

$A_p = \frac{\pi}{4} D^2$ = cross-sectional area of pipe, sq ft

C_p = unit heat capacity of water, Btu/lb deg F

D = inside diameter of tube, ft

$G = \frac{W_T}{A_p}$ = weight flow per unit area, lb/hr ft²

g = gravitational force per unit mass = $\frac{4.17 \times 10^8 \text{ lb}}{\frac{(\text{lb hr}^2)}{(\text{ft})}}$

L = length of tube, ft

L_H = total heated length, ft

L_T = total length between pressure taps, ft

n = exponent, defined in text

P = absolute pressure, psia

q = rate of heat transfer, Btu/hr

r_1 = multiplier of $\frac{G^2}{g}$, defined in text, cu ft per lb

r_2 = multiplier of $\frac{G^2}{g}$, defined in text, cu ft per lb

r = value of multiplier of $\frac{G^2}{g}$ between r_1 and r_2, cu ft per lb

R_g = fraction of pipe volume filled by vapor

R_l = fraction of pipe volume filled by liquid

t_s = saturation temperature, deg F

t_1 = inlet temperature, deg F

Δt = average temperature difference between outside of tube and water, as defined and given in Table 2 of reference (1), deg F

U = over-all heat-transfer coefficient between outside of tube and water, Btu/hr ft² deg F

v_g = vapor velocity during two-phase flow, fph

v_l = liquid velocity during two-phase flow, fph

v_0 = liquid velocity entering tube, fph

$\overline{V}_l$ = specific volume of saturated liquid, cu ft per lb

$\overline{V}_g$ = specific volume of saturated vapor, cu ft per lb

W_g = weight flow of vapor, lb per hr

W_l = weight flow of liquid, lb per hr

$W_T = W_g + W_l$ = total weight flow, lb per hr

x = quality of steam at any point in tube, based on weight flow

x_e = exit quality of steam, based on weight flow

y = length defined in Appendix

z = length defined in Appendix

ΔP_a = pressure drop due to acceleration of fluid, psf

ΔP_0 = pressure drop in flow circuit for flow of saturated water at rate W_T and pressure P, psf

ΔP_{TPF} = frictional pressure drop, psf

ΔP_{TP} = total pressure drop in flow circuit for forced-circulation boiling of water at pressure P, total weight flow W_T, and exit quality x_e, psf

$\left(\frac{\Delta P}{\Delta L}\right)_{\text{TPF}}$ = two-phase pressure gradient, psf/ft

$\left(\frac{\Delta P}{\Delta L}\right)_g$ = pressure gradient assuming only vapor phase flowing, psf/ft

$\left(\frac{\Delta P}{\Delta L}\right)_l$ = pressure gradient assuming only liquid phase flowing, psf/ft

$\left(\frac{dP}{dL}\right)_{\text{TPF}}$ = local two-phase pressure gradient, psf/ft

$\left(\frac{dP}{dL}\right)_l$ = local pressure gradient assuming only liquid phase flowing, psf/ft

$\left(\frac{\Delta P}{\Delta L}\right)_0 = \left(\frac{dP}{dL}\right)_0$ = pressure gradient for liquid only flowing at rate W_T, psf/ft

μ_g = viscosity of saturated vapor, lb/hr ft

μ_l = viscosity of saturated liquid, lb/hr ft

Φ_{gtt} = parameter discussed in text

Φ_{ltt} = parameter discussed in text

$\chi_{tt} = \left(\frac{\overline{V}_l}{\overline{V}_g}\right)^{\frac{1}{2-n}} \left(\frac{\mu_l}{\mu_g}\right)^{\frac{n}{2-n}} \left(\frac{W_l}{W_g}\right)$ = parameter discussed in text

Subscripts:

H = heated

T = total

l = liquid

g = vapor

s = saturated

1 = entrance

TP = two phase

TPF = two phase, frictional

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Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-113.

0 = zero quality (100 per cent liquid)
tt = turbulent-turbulent

INTRODUCTION

In a number of engineering flow systems it is important for the designer to be able to predict the pressure drop occurring during the forced-circulation boiling of water. In most of the calculations described in the literature, the two phases, water and steam, are considered as a uniform homogeneous mixture with a calculable specific volume, and the frictional pressure drop is calculated by means of the usual Weisbach or Fanning equations. The principal difficulty in these calculations arises in the estimation of the friction factor, since a Reynolds number for the mixture is difficult to define. One approach to the problem was suggested by Davidson, Hardie, Humphreys, Markson, Mumford, and Ravese (1),[3] who used a modified Reynolds modulus and thereby accomplished a reasonably reliable mode of correlation for the friction factor during two-phase flow. McAdams, Woods, and Heroman (2), utilized a somewhat different approach, also with encouraging results.

A completely different mode of approach has been suggested in a recent series of papers (3, 4, 5) in which the pressure drop during two-phase flow is related to the pressure drop occurring if only a single phase flowed in the pipe. Although the experimental data presented in these references apply specifically to isothermal flow of air and various other liquids, the data were purposely presented in a tentatively generalized form, which should make the results applicable to water-steam mixtures.[4]

It is the purpose of this paper to combine the data in references (3, 4, 5) with those of references (1) and (2) in order to establish a new approach to the problem of pressure drop during forced-circulation boiling. As will be noted, the methods proposed are tentative, being based upon a number of hypotheses requiring experimental verification. It is the hope of the authors, however, that the paper will stimulate discussion and further investigation of the problem.

It is postulated that the pressure drop resulting from the flow of a boiling mixture, when the pressure drop across the tube is small compared to the absolute pressure, is made up of two parts: (*a*) the pressure drop due to the frictional forces acting during two-phase flow; and (*b*) the pressure drop resulting from the rate of increase of momentum of the mixture as it flows through the tube and vaporizes. These two components of the pressure drop will be discussed.

FRICTIONAL PRESSURE DROP

In reference (3) it was shown that two-phase flow can occur in four general forms:

1 The flow of both liquid and vapor can be turbulent.

2 The flow of both liquid and vapor can be viscous.

3 The flow of the liquid can be viscous and the vapor turbulent.

4 The flow of the liquid can be turbulent and the vapor viscous.

For all practical purposes any normal forced-circulation-boiler design would involve only the first of these flow mechanisms, namely, the flow will be "turbulent-turbulent."

In reference (3) it was shown that for isothermal two-phase flow the frictional pressure drop[5] can be calculated as follows[6]

$$\left(\frac{\Delta P}{\Delta L}\right)_{\text{TPF}} = \left(\frac{\Delta P}{\Delta L}\right)_{g} \Phi_{gtt}^{2} \ldots\ldots\ldots\ldots\ldots [1]$$

where $\left(\frac{\Delta P}{\Delta L}\right)_{\text{TPF}}$ is the frictional pressure drop due to two-phase flow, $\left(\frac{\Delta P}{\Delta L}\right)_{g}$ is the pressure drop if only the vapor is flowing in the pipe and Φ_{gtt} is a parameter obtained experimentally, (3, 5) and found to be correlated by means of the dimensionless parameter, χ_{tt} where

$$\chi_{tt} = \left(\frac{V_l}{V_g}\right)^{\frac{1}{2-n}} \left(\frac{\mu_l}{\mu_g}\right)^{\frac{n}{2-n}} \left(\frac{W_l}{W_g}\right) \ldots\ldots\ldots\ldots [2]$$

The exponent n is obtained by plotting the single-phase pressure drop versus weight flow on log-log paper. The slope of the curve is equal to $2 - n$. For the data in reference (1) a value of n between 0.2 and 0.25 was found. A value of $n = 0.25$ was used in the calculations.

In reference (5) the analysis presented in reference (3) was extended and the two-phase pressure drop was also shown to be equal to

$$\left(\frac{\Delta P}{\Delta L}\right)_{\text{TPF}} = \left(\frac{\Delta P}{\Delta L}\right)_{l} \Phi_{ltt}^{2} \ldots\ldots\ldots\ldots\ldots [3]$$

where $\left(\frac{\Delta P}{\Delta L}\right)_{l}$ is the pressure drop resulting if only liquid flowed in the pipe. In the remainder of the paper it will be found convenient to utilize Equation [3] for the calculation of two-phase pressure drop. The relation between Φ_{gtt} and Φ_{ltt} is given by (5)

$$\Phi_{ltt} = \frac{\Phi_{gtt}}{\chi_{tt}^{\frac{2-n}{2}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [4]$$

In addition, in reference (5), the curves of Φ_{gtt} and Φ_{ltt} were reevaluated, and found to differ slightly from those presented in reference (3). On the basis of the data in reference (5) therefore the curve of Φ_{ltt} versus χ_{tt} was established, as shown in Fig. 1.

It is proposed to use the curve in Fig. 1 as follows: Assume that at each point along the tube in which forced-circulation boiling is taking place, thermodynamic equilibrium exists. Also assume that at each point along the tube the curve shown in Fig. 1 can be applied. Then at any point

$$\left(\frac{dP}{dL}\right)_{\text{TPF}} = \left(\frac{dP}{dL}\right)_{l} \Phi_{ltt}^{2} \ldots\ldots\ldots\ldots\ldots [5]$$

At each point along the tube the properties of the vapor and liquid are known (6). In addition, the quality of the water-steam mixture is defined as

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[3] Numbers in parentheses refer to the Bibliography at the end of the paper.

[4] During the simultaneous flow of a liquid and gaseous phase through a tube, under certain conditions, the phases are well separated; under other conditions part of the liquid may move in small droplets as a fog, the remaining liquid clinging to the walls of the tube. All other conditions being the same, the latter form of flow is more likely to occur during boiling than during the isothermal flow of air and other liquids. This probable change in flow pattern between nonboiling and boiling flow means that the utilization of the isothermal data from references (3, 4, 5) for the prediction of pressure drop during forced-circulation boiling, is not entirely justified. Since, however, "fog" formation is also noted in the isothermal two-phase flow, the error may not be large. The final comparison between predicted and measured pressure drops, discussed later in the paper, apparently bears out this contention.

[5] During the isothermal flow experimental runs, (3, 5), frictional pressure drop only was obtained, since no change in the momentum of the fluids took place. It is postulated therefore that the extension of the isothermal data to the case of forced-circulation boiling will yield the frictional pressure drop. The pressure drop due to momentum changes must be added to the frictional pressure drop, as is discussed later.

[6] See Nomenclature.

$$x = \frac{W_g}{W_g + W_l} \quad \text{[6]}$$

Thus the parameter χ_{tt} is known, once the quality is known, since (using a value of $n = 0.25$)

$$\chi_{tt} = \left(\frac{\bar{V}_l}{\bar{V}_g}\right)^{0.571}\left(\frac{\mu_l}{\mu_g}\right)^{0.143}\left(\frac{1}{x} - 1\right) \quad \text{[7]}$$

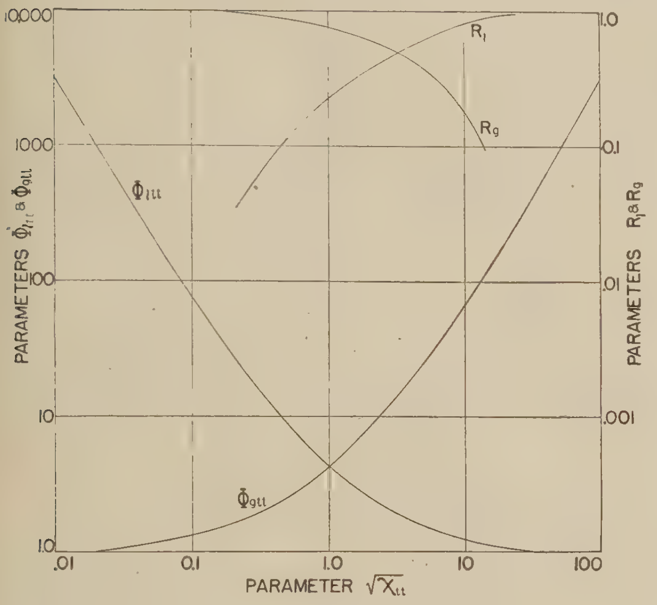

FIG. 1 PLOT OF Φ_{ltt}, Φ_{gtt}, R_l AND R_g, VERSUS $\sqrt{\chi_{tt}}$
[Data from references (3) and (5).]

As a first approximation, throughout the remainder of this analysis, it will be assumed that a linear relationship exists between x and L. Thus the value of χ_{tt} is known at any point along the tube once the exit quality is established.

In addition, since

$$\left(\frac{dP}{dL}\right)_l = \left(\frac{dP}{dL}\right)_0\left(\frac{W_l}{W_T}\right)^{1.75} = \left(\frac{dP}{dL}\right)_0 (1 - x)^{1.75} \quad \text{[8]}$$

where $\left(\frac{dP}{dL}\right)_0$ is the pressure gradient for the flow of 100 per cent liquid, one can write

$$\frac{\left(\frac{dP}{dL}\right)_{TPF}}{\left(\frac{dP}{dL}\right)_0} = (1 - x)^{1.75}\,\Phi_{ltt}^2 \quad \text{[9]}$$

The ratio $\left(\frac{dP}{dL}\right)_{TPF} \Big/ \left(\frac{dP}{dL}\right)_0$ versus x now can be plotted readily for any specific pressure, since the variables in Equation [9] are all functions of P and x only.

Having such a plot, the pressure drop for any given pipe at any given mean pressure P can be calculated as follows

$$\frac{\Delta P_{TPF}}{\Delta P_0} = \frac{1}{x_e}\int_0^{x_e}\left[\frac{\left(\frac{dP}{dL}\right)_{TPF}}{\left(\frac{dP}{dL}\right)_0}\right]dx \quad \text{[10]}$$

where ΔP_{TPF} is the two-phase pressure drop in the pipe with mean pressure P, and exit quality x_e and ΔP_0 is the pressure drop across the same tube, assuming no vaporization at all to occur (flow of 100 per cent liquid). The latter pressure drop is readily calculated. The term on the right of the equal sign is the mean ordinate for x_e on the curves of $\left(\frac{dP}{dL}\right)_{TPF} \Big/ \left(\frac{dP}{dL}\right)_0$ versus x and is thus easily determined graphically.

The steps outlined were carried out, starting with Fig. 1, and a set of curves $\frac{\Delta P_{TPF}}{\Delta P_0}$ versus x_e for various pressures obtained. Two discrepancies were immediately noted, as follows:

1 The high-pressure data of reference (1) were definitely overestimated, the error increasing as the pressure increased.

2 As the critical pressure (3206 psia) was reached, by definition the ratio of $\frac{\Delta P_{TPF}}{\Delta P_0}$ should have approached unity, but this was not the case, a value of about 5 being approached.

It was apparent that the data used to establish Fig. 1 could not be extrapolated directly to the critical point. Another parameter, a function of pressure, must enter the correlation of Φ_{ltt} versus χ_{tt}. Since the data utilized to obtain the curves in Fig. 1 were mainly obtained with air and water atmospheric pressure, comparison of the properties of air and water and water vapor and water indicated that the curve in Fig. 1 should probably apply to water vapor and water at about 1 atm abs pressure. The question was now to establish the curves for other pressures.

The limiting curve for the critical point can be established directly by the following argument: The two-phase pressure drop is, from Equation [3]

$$\left(\frac{\Delta P}{\Delta L}\right)_{TPF} = \left(\frac{\Delta P}{\Delta L}\right)_l \Phi_{ltt}^2 \quad \text{[11]}$$

At the critical point, however, since there is no distinction between phases

$$\left(\frac{\Delta P}{\Delta L}\right)_{TPF} = \left(\frac{\Delta P}{\Delta L}\right)_0 \quad \text{[12]}$$

but, from Equation [8]

$$\left(\frac{\Delta P}{\Delta L}\right)_l = \left(\frac{\Delta P}{\Delta L}\right)_0 (1 - x)^{1.75} \quad \text{[13]}$$

Thus combining Equations [11], [12], and [13], the value of Φ_{ltt} at the critical point is

$$\Phi_{ltt} = \frac{1}{(1 - x)^{0.875}} \quad \text{[14]}$$

However, at the critical point Equation [2] becomes

$$\chi_{tt} = \left(\frac{1}{x} - 1\right) \quad \text{[15]}$$

Combining Equations [14] and [15] gives the relation between Φ_{ltt} and χ_{tt} at the critical point

$$\Phi_{ltt} = \left(\frac{\chi_{tt} + 1}{\chi_{tt}}\right)^{0.875} \quad \text{[16]}$$

The curve of Φ_{ltt} versus χ_{tt} for the critical pressure is now known. The remaining curves at intermediate pressures[7] were established by trial and error, using the data from reference (1) as a guide for fitting the curves. The resulting plot is shown in Fig. 2.

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[7] The basic parameter associated with the various curves is not known.

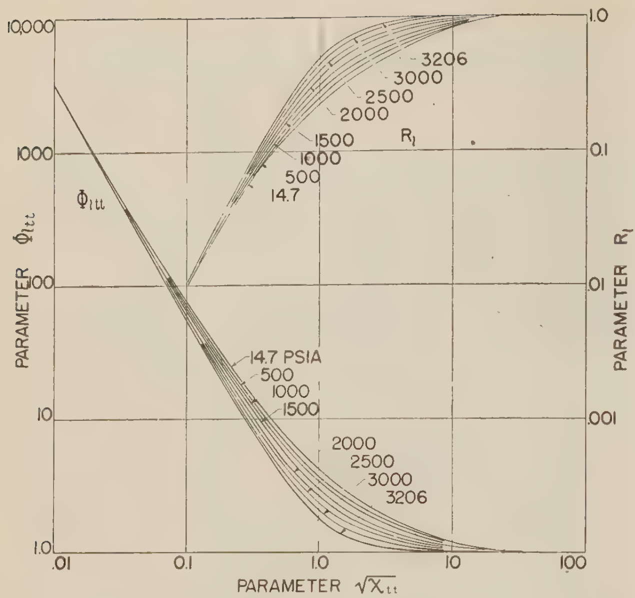

Fig. 2 Plot of Parameters Φ_{ltt} and R_l Versus Parameter $\sqrt{X_{tt}}$ for Various Pressures From 1 Atm Abs Pressure to Critical Pressure for Water and Water Vapor

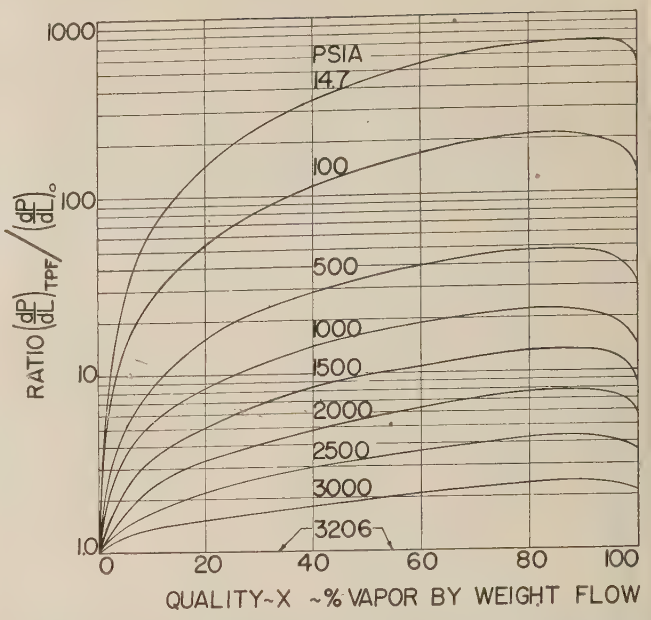

Fig. 3 Ratio of Local Two-Phase Pressure Gradient to Pressure Gradient for 100 Per Cent Liquid Flow as a Function of Quality and Pressure

Having established the curves of Φ_{ltt} versus X_{tt} for a number of pressures, the steps outlined in the first part of this paper were followed, and curves of $\left(\frac{dP}{dL}\right)_{\text{TPF}} \Big/ \left(\frac{dP}{dL}\right)_0$ were obtained as shown in Fig. 3. Integration of these curves, as indicated by Equation [10], gives the final curves shown in Fig. 4. For convenience, numerical values are given in Table 1.

With these curves, which are tentative in nature, it is proposed that the frictional pressure drop during forced-circulation boiling can be quickly determined in the following manner: A calculation of the pressure drop, assuming no evaporation, ΔP_0, is made by the usual methods, including all bends, etc., which may exist in the flow circuit. Then, knowing the average pressure in the evaporator section and the exit quality, the frictional pressure drop during forced-circulation boiling is determined by multiplying ΔP_0 by the ratio $\frac{\Delta P_{\text{TPF}}}{\Delta P_0}$ obtained from Fig. 4.

TABLE 1 VALUES OF $\frac{\Delta P_{\text{TPF}}}{\Delta P_0}$ AS A FUNCTION OF x_e AND P

Steam quality, per cent by weight flow	Pressure, psia							
	14.7	100	500	1000	1500	2000	2500	3206
1	4.7	2.8	1.79	1.45	1.28	1.17	1.08	1.00
5	16.5	7.4	3.42	2.30	1.77	1.43	1.21	1.00
10	33.0	13.8	5.13	3.10	2.23	1.72	1.39	1.00
20	68.5	25.9	8.90	4.92	3.18	2.27	1.70	1.00
30	108	39.5	12.1	6.40	4.00	2.68	1.90	1.00
40	152	52.5	15.1	7.70	4.74	3.15	2.20	1.00
50	198	65.0	18.0	8.96	5.40	3.55	2.48	1.00
60	246	76.0	21.2	10.3	6.10	3.92	2.62	1.00
70	293	87.2	24.2	11.9	6.93	4.36	2.82	1.00
80	337	97	27.3	13.2	7.62	4.70	2.95	1.00
90	377	108	29.2	14.0	8.00	4.98	3.10	1.00
100	408	118	31.0	14.9	8.50	5.26	3.22	1.00

The method discussed in the foregoing gives the friction pressure drop during forced-circulation boiling. The pressure drop due to the rate of increase of momentum of the material passing through the tube must now be calculated in order to obtain the total pressure drop.

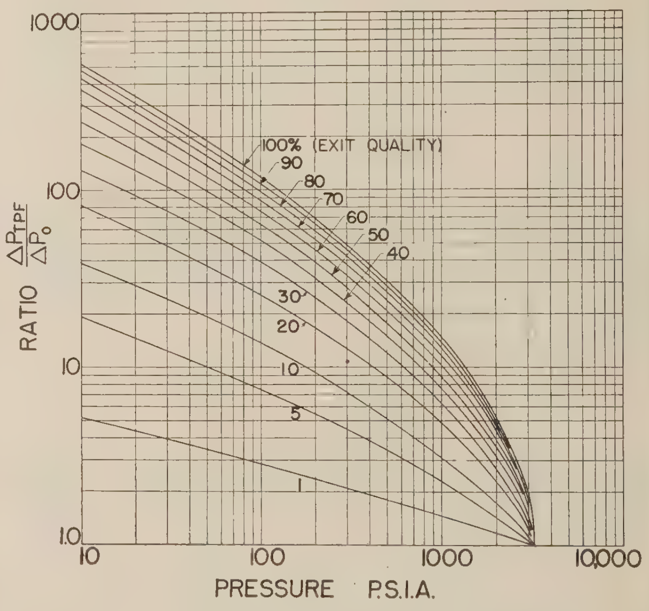

Fig. 4 Ratio ΔP_{TPF} to ΔP_0 as a Function of Exit Quality and Absolute Pressure

Pressure Drop Due to Momentum Changes

If the pressure drop across the tube is small compared to the absolute pressure, the flow is effectively incompressible. In other words, although the specific volume of the mixture changes over wide limits, the specific volume of each phase is substantially constant along the tube.

For these conditions it is postulated that the pressure drop due to the change in specific volume of the mixture can be calculated as follows

$$A_p \Delta P_a = \text{rate of change of momentum}$$

$$= \frac{W_l v_l}{g} + \frac{W_g v_g}{g} - \frac{W_T v_0}{g} \qquad [17]$$

where W_l, W_g, and W_T have been defined previously, v_l is the liquid velocity leaving the tube, v_g is the vapor velocity leaving the tube, and v_0 is the liquid velocity entering the tube, ΔP_a is the pressure drop due to momentum changes.

As was discussed in the Introduction, two extreme cases of exit conditions can now exist, the actual condition probably lying between the two extremes:

1 Liquid and vapor completely mixed (fog).
2 Liquid and vapor completely separated.

The first case is that usually utilized in the literature and can be expressed as follows, since $v_g = v_l$

$$\Delta P_a = \frac{G^2}{g}\left[(1 - x) + x\left(\frac{\overline{V}_g}{\overline{V}_l}\right) - 1\right]\overline{V}_l = r_1\frac{G^2}{g}\ldots[18]$$

The latter case can be readily evaluated if v_g and v_l are known. In reference (5) curves are given which, for isothermal two-phase flow, allow the estimation of the per cent of pipe filled with liquid, R_l, and with vapor, R_g, once the parameter χ_{tt} is known. These curves are shown in Fig. 1.

One may then write, from Equation [17]

$$\Delta P_a = \frac{G^2}{g}\left[\frac{(1 - x)^2}{R_l} + \frac{x^2}{R_g}\left(\frac{\overline{V}_g}{\overline{V}_l}\right) - 1\right]\overline{V}_l = r_2\frac{G^2}{g}\ldots[19]$$

The question again arises as to the situation at the critical point. Since at this point $\Delta P_a = 0$ and $\overline{V}_g/\overline{V}_l = 1$, one obtains from Equation [19]

$$R_l = (1 - x) \text{ (at critical point)}$$
$$R_g = x \qquad \text{ (at critical point)}$$

Since the relation between χ_{tt} and x is known at the critical point from Equation [15], the curve of R_l versus χ_{tt} at the critical point can be calculated readily. This was done as shown in Fig. 2. There is appreciable difference between the curve at the critical point and the experimental curves obtained at 14.7 psia. A series of curves were interpolated arbitrarily for the various intermediate pressures, since no data for R_l exist at higher pressures. Even if these curves are not exact, they will yield results which are qualitatively correct. Having the curves in Fig. 2, it is an easy matter to obtain the curves in Fig. 5, where χ_{tt} has been replaced by x, with pressure as a parameter. This curve indicates the fraction of pipe filled by liquid and vapor at various qualities and pressures. Experimental verification is required, particularly at the higher pressures.

From Fig. 5 and Equation [19], the multiplier r_2 of G^2/g was plotted as a function of pressure and quality in Fig. 6. For convenience numerical values are given in Table 2.

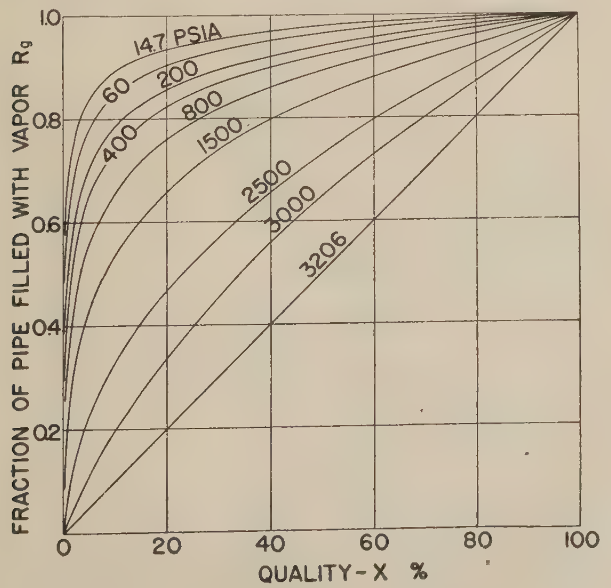

FIG. 5 PER CENT OF PIPE VOLUME FILLED WITH LIQUID AS A FUNCTION OF QUALITY AND ABSOLUTE PRESSURE

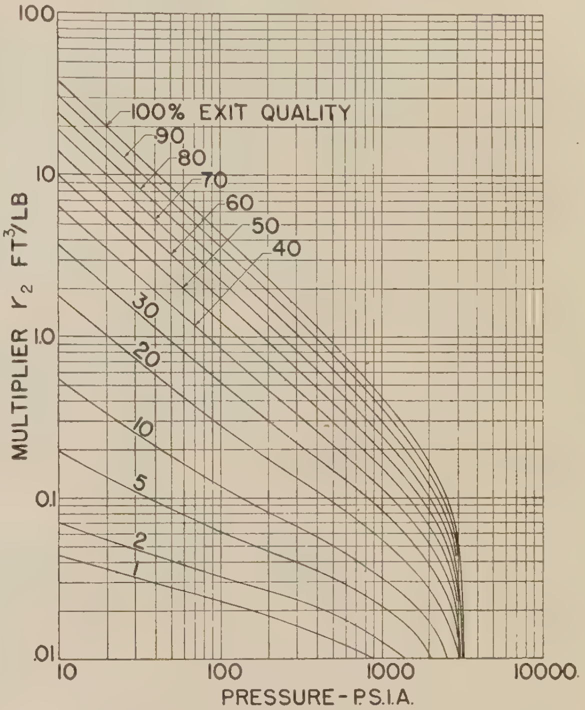

FIG. 6 MULTIPLIER r_2 VERSUS ABSOLUTE PRESSURE FOR VARIOUS EXIT QUALITIES

(The pressure drop due to acceleration of fluid during evaporation equals $r_2\frac{G^2}{g}$.)

The final value of ΔP_a will probably lie between the limits set by Equations [18] and [19], since the water-vapor mixture leaving the heating section will be partially in the form of fog and partially separate liquid and vapor.

TABLE 2 VALUES OF MULTIPLIER r_2 AS A FUNCTION OF x_e AND P

Steam quality, per cent by weight flow	Pressure, psia							
	14.7	100	500	1000	1500	2000	2500	3206
1	0.04	0.023	0.0130	0.0093	0.0067	0.0041	0.0021	0
5	0.16	0.068	0.0316	0.0211	0.0153	0.0100	0.0064	0
10	0.41	0.118	0.0498	0.0313	0.0227	0.0163	0.0100	0
20	1.30	0.280	0.093	0.054	0.037	0.026	0.017	0
30	2.70	0.522	0.146	0.084	0.054	0.037	0.025	0
40	4.60	0.850	0.209	0.112	0.074	0.049	0.033	0
50	7.03	1.250	0.291	0.150	0.096	0.064	0.043	0
60	9.95	1.730	0.384	0.193	0.121	0.080	0.053	0
70	13.40	2.27	0.494	0.241	0.149	0.098	0.064	0
80	17.20	2.90	0.618	0.296	0.180	0.117	0.076	0
90	21.80	3.63	0.762	0.360	0.215	0.139	0.088	0
100	26.7	4.40	0.903	0.420	0.253	0.162	0.102	0

RECAPITULATION

The pressure drop during the forced-circulation boiling of water can now be expressed as

$$\Delta P_{TP} = \Delta P_0\left(\frac{\Delta P_{TPF}}{\Delta P_0}\right) + r\frac{G^2}{g}\ldots\ldots\ldots\ldots[20]$$

The postulates and restrictions upon which the evaluation of $\frac{\Delta P_{TPF}}{\Delta P_0}$ and r are based, are as follows:

1 The validity of extending the curve of Φ_{ltt} versus χ_{tt} obtained for flow of air and various other liquids, to boiling water is postulated.

2 The validity of a point-to-point evaluation of Φ_{ltt} and $\left(\frac{dP}{dL}\right)_l$ and the consequent integration is postulated.

3 The validity of extrapolating the curves of Φ_{ltt} and R_l to the critical point as suggested in the paper is postulated.

4 A linear relationship between quality and L is postulated. Radical variation from this relationship requires new local pressure gradients to be calculated.

5 The curves are strictly applicable only to a horizontal tube of constant diameter.

DISCUSSION

The method described was checked by attempting to predict the experimental data of references (1) and (2).

The significance of the prediction of the data of reference (1) can be questioned, since these data were used to help establish the curves in Fig. 4. However, it must be remembered that the data in reference (1) cover exit qualities from 6 per cent to 100 per cent and pressures from 500 to 3000 psia. The reasonable correlation between predicted and experimental pressure drop shown in Fig. 7 for this rather large range of data suggests that the curves in Fig. 4 may be generally applicable.

The pressure drop due to the acceleration of the fluid was a small fraction of the frictional pressure drop for the data in reference (1) and therefore no significant difference between the calculations based on r_1 and r_2 was noted. For those few points where the difference is noticeable, the range of predicted values is shown by a vertical line through the point. A sample calculation is shown in the Appendix.

The lack of correlation at the lower pressure drops may be a result of the coiled form of the test pipes, since at low flow rates the liquid may have collected at the bottom of the coil. In addition, the relation between x and L may have been far from linear at the low flow rates. For these reasons the data reported in reference (1) for larger pipes which gave very low pressure drops, were not included in the correlation shown in Fig. 7. The data for 1-in. pipe could not be calculated, since insufficient data for calculating ΔP_0 were presented.

The data in reference (2) were obtained at pressures between 18 psia and 25 psia, for qualities between 4 and 95 per cent. The pressure drop due to acceleration was appreciable for these runs, being of the same order of magnitude as the frictional pressure drop. Fig. 8 shows the correlation between measured and predicted pressure drops. The predicted values are shown by a vertical line, the lower limit being the value based upon the correction r_2, and the upper limit the value obtained by using the correction r_1. It is noted that on the average, the measured value lies between these two limits. Further, it was observed that the runs in which the vaporization was most gradual (occurring in four passes of the evaporator), the correction r_2 gave the best correlation, while for these runs in which vaporization was more rapid (occurring in two or three passes), somewhat better correlation was obtained by using the multiplier r_1.

CONCLUSIONS

A tentative method for the rapid calculation of pressure drop during forced-circulation boiling of water has been presented. Comparison of predicted and measured pressure drops with pressures from 18 to 3000 psia and exit qualities from 4 to 100 per cent indicates that the proposed method has promise. The method, however, is based upon a meager amount of data and requires further experimental verification before it can be considered valid. If the proposed method is found reliable, extension to the calculation of pressure drop during the vaporization or condensation of liquids other than water should be possible.

ACKNOWLEDGMENTS

The authors wish to acknowledge the aid of Mrs. Florence Adamson who performed most of the calculations for this paper.

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Appendix

SAMPLE CALCULATION

Study of the data in reference (1) reveals that (*a*) the distance between pressure taps was greater than the length of the heating section; and (*b*) water below the saturation temperature entered the heating section. As a consequence, boiling occurred in only a part of the length between pressure taps. In order to compare measured pressure drops with predicted pressure drops, the length of the tube in which boiling took place must be estimated.

As an example, Run 26B, from reference (1), will be calculated. The pertinent data are as follows:

Diameter of tube = 0.5 in. ID × 0.75 in. OD
Pressure = 1500 psia
Inlet temperature = 587 F
Outlet temperature = 596 F (measured)
Saturation temperature = 596.2 F (theoretical)
Exit quality = 53 per cent (by weight flow)
Rate of flow = 737 lb per hr

For purposes of this analysis, the following definitions are made:

L_H = total heated length of coil
L_T = total coil length between pressure taps
$z = \frac{L_T - L_H}{2}$ = length of tubing at each end between pressure tap and heated portion of coil
y = length of coil required to raise water to saturation temperature

From reference (1) for Run 26B

$$L_H = 20.3 \text{ ft}; \quad L_T = 25.6 \text{ ft}; \quad z = 2.65 \text{ ft}$$

Note that y is a function of the weight flow, of the difference between inlet and saturation temperature, and of the rate of heat transfer; therefore y must be determined individually for all test points.

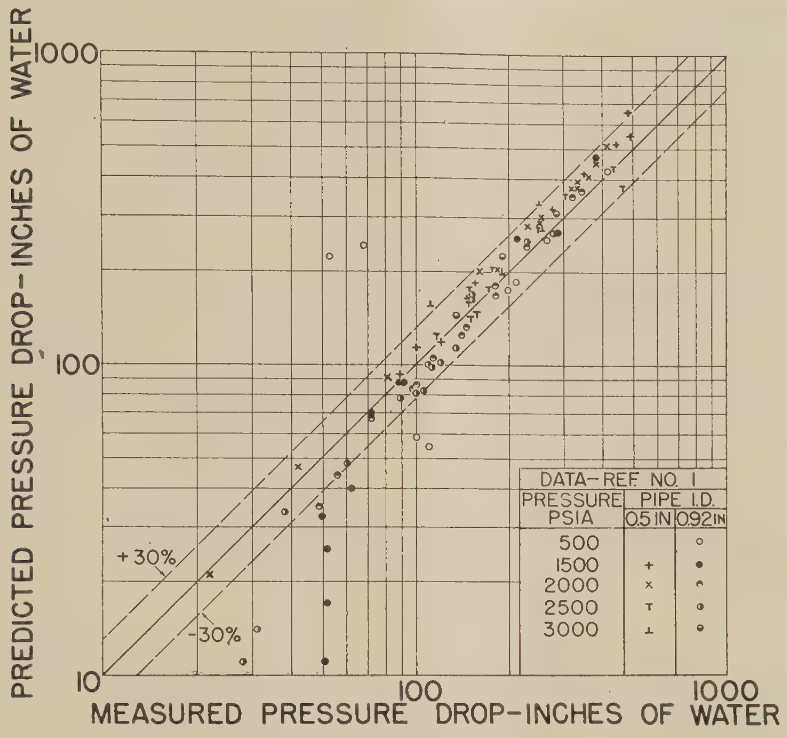

FIG. 7 PREDICTED VERSUS MEASURED PRESSURE DROP FOR 0.5-IN. AND 0.92-IN-DIAM TUBES

(Data from reference 1. Pressures from 500 to 3000 psia, and exit qualities from 6 per cent to 100 per cent.)

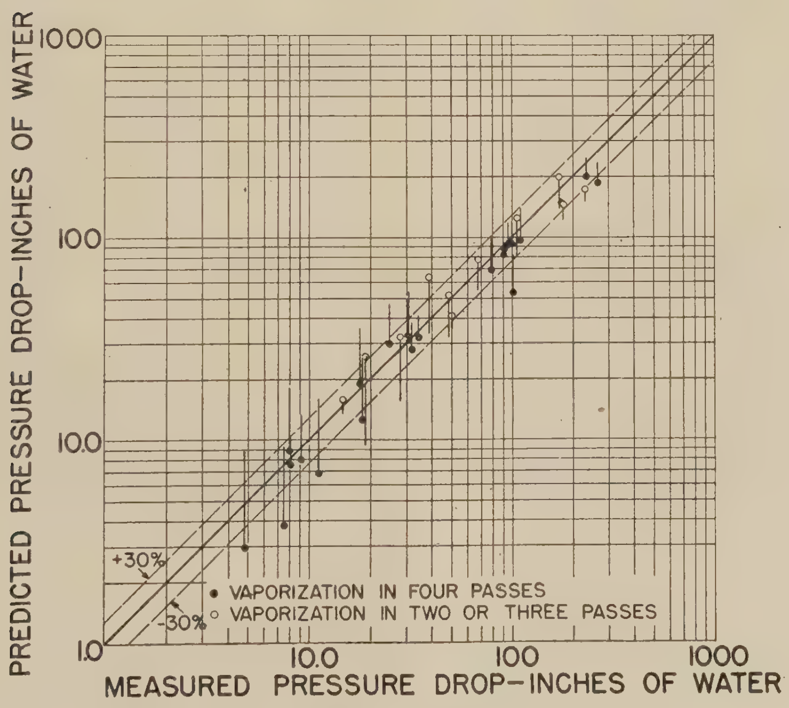

FIG. 8 PREDICTED VERSUS MEASURED PRESSURE DROP FOR 1.06-IN-DIAM TUBE

(Data from reference 2. Pressures from 18 to 25 psia, and exit qualities from 4 per cent to 95 per cent. Vertical lines indicate spread in predicted values resulting from use of multipliers r_1 and r_2.)

The heat transferred in length y is

$$q = UA_y \Delta t$$

where[8]

$$A_y = \pi D y$$

Also

$$q = W_T C_p (t_s - t_1)$$

Thus equating these expressions for q

$$W_T C_p (t_s - t_1) = UA_y \Delta t$$

For any run, all the quantities in the foregoing equation are known except U and A_y. The value of U was estimated by plotting

$$\frac{1}{U} \text{ versus } \frac{1}{W_T^{0.8}}$$

for all the 100 per cent liquid runs. A mean curve through these points gave the equation

$$\frac{1}{U} = 0.000498 + \frac{0.212}{W_T^{0.8}}$$

Thus

$$y = \frac{W_T C_p \, (t_s - t_1)}{\pi D \Delta t} \left(0.000498 + \frac{0.212}{W_T^{0.8}} \right)$$

Substituting values for Run 26B

$$y = 2.45 \text{ ft}$$

Now

$$\Delta P_{\text{TPF}} = \left(\frac{\Delta P}{\Delta L}\right)_0 (y + z) + \left(\frac{\Delta P}{\Delta L}\right)_0 \left(\frac{\Delta P_{\text{TPF}}}{\Delta P_0}\right) (L_T - y - z)$$

which may be written as

$$\Delta P_{\text{TPF}} = \left(\frac{\Delta P}{\Delta L}\right)_0 \left[(y + z) \left(1 - \frac{\Delta P_{\text{TPF}}}{\Delta P_0}\right) + \left(\frac{\Delta P_{\text{TPF}}}{\Delta P_0}\right) L_T \right]$$

The evaluation of $\left(\frac{\Delta P}{\Delta L}\right)_0$ may be accomplished by two methods. A calculated value might be obtained by application of the "Fanning" equation with a proper choice of friction factor and a correction applied for the spiral form of the coil. However, the uncertain nature of the latter two factors led the authors to use a plot of the ΔP_0 versus W_T data reported in the liquid heating runs of reference (1). This is the same plot from which the n of Equation [2] was obtained.

For Run 26B

$$\left(\frac{\Delta P}{\Delta L}\right)_0 = 1.2 \text{ in. } H_2O \text{ per ft of tube}$$

From Fig. 4, at 1500 psia and 53 per cent quality

$$\left(\frac{\Delta P_{\text{TPF}}}{\Delta P_0}\right) = 5.65$$

Then, solving the foregoing equation for ΔP_{TPF}

$$\Delta P_{\text{TPF}} = 145.3 \text{ in. } H_2O$$

Assuming a homogeneous mixture (fog) of liquid and vapor phases, i.e., $v_g = v_l$

$$\Delta P_a = r_1 \frac{G^2}{g} \quad \text{[18]}$$

Substituting and solving

$$r_1 = 0.133$$

and

$$\Delta P_{a1} = 18 \text{ in. } H_2O$$

If instead, the two phases are assumed to flow separately

$$\Delta P_a = r_2 \frac{G^2}{g} \quad \text{[19]}$$

From Fig. 6

$$r_2 = 0.10$$

therefore

$$\Delta P_{a2} = 14 \text{ in. } H_2O$$

However

$$\Delta P_{\text{TP}} = \Delta P_{\text{TPF}} + \Delta P_a$$

Therefore

$$\Delta P_{\text{TP(1)}} = 163.3 \text{ in. } H_2O$$

while

$$\Delta P_{\text{TP(2)}} = 159.3 \text{ in. } H_2O$$

From reference (1)

$$\Delta P_{\text{TP(measured)}} = 148 \text{ in. } H_2O$$

The data in reference (2) were treated in a similar manner. The lengths in which evaporation occurred were determined from detailed data given in reference (2*b*). This latter reference also gave pressures and quality at the end of each pass as well as the over-all pressure drop and quality at exit. Therefore it was possible to use the intermediate points as independent runs to obtain a greater number of points for correlation, Fig. 8.

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[8] The effective heat-transfer area in the tests in reference (1) was only a fraction (probably between 0.50 and 0.60) of the actual heat-transfer area (A_y) because of the nonuniform heating of the tube. For the purposes of calculation, however, the total inside heat-transfer surface was utilized in evaluating U. This does not introduce any error in the final calculated value of y, since the product UA enters all calculations, rather than U per se.

Analysis of Tests on Positive-Displacement Meters for Liquid Hydrocarbons

By E. E. AMBROSIUS,[1] STATE COLLEGE, PA.

This paper gives an amplification of results of tests on one meter and represents a method of analysis of data from the tests conducted by the ASME Special Research Committee on Fluid Meters and the API Topical Committee on Volumeter Research, to determine the characteristics of displacement-type mechanical meters when measuring liquid hydrocarbons. It is a continuation of an earlier paper,[2] and presents data with a method of further analysis beyond that made in the preliminary study. The early paper discussed the results in a general way. A more thorough study of the data on a particular meter, such as herein presented, can point the way toward close control of meter-performance characteristics for any particular design.

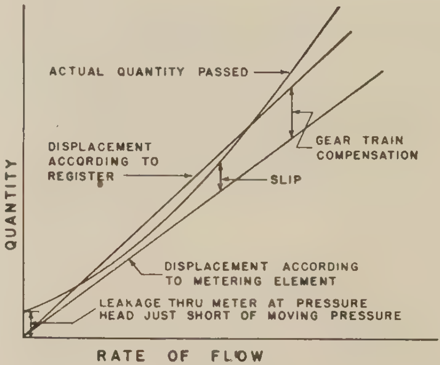

Fig. 1 General Displacement-Meter Characteristics

Purpose

There is need that pertinent information relative to the method of analysis of performance data for positive-displacement meters be given. It is not the purpose of this paper to show any meter to give good or bad performance over any or all its operating range, but rather, it is intended to show a method of analysis and the interpretation of results, based upon experience gained in testing these meters with four different liquid hydrocarbons at four different temperatures.

The method of analysis is based upon the fact, and as the test data revealed, that all displacement meters have common characteristics and respond to similar conditions in somewhat the same manner, but in varying degree. This is not a startling observation since all meters may be considered as fluid motors, operating against a light load, primarily due to friction and the meter index. Inasmuch as the various meters are manufactured with varying degrees of precision, have different metal composition and combinations in the case and internal mechanism, and are not geometrically similar, one would naturally expect different degrees of responsiveness to similar conditions imposed upon the several different types.

General Theory

It is well to think of a meter as a hydraulic motor, requiring a small pressure drop to operate. The main factors which cause the pressure drop necessary to operate the meter, are fluid friction, friction of the metering element, and meter index. This pressure drop across the meter will cause a certain amount of oil to pass unmetered through the small clearance between piston and cylinder. The oil that passes through the meter in this manner is referred to as "slip."

The general characteristics of a meter can best be shown by the use of a graph, as in Fig. 1. It will be noted that the rate of flow is plotted against the quantity of oil which actually passes through the meter. If the slippage of the oil past the working parts did not occur, the rate of flow multiplied by the time would give the quantity that passed through the meter. This can be stated another way, namely, the quantity passed is equal to the displacement of the metering element per cycle times the total number of cycles for a given length of time. Flow under this condition could be represented by the straight line referred to as "Displacement According to Metering Element." Since there is slip, the actual curve plotted from test data, as proof of the meter, may actually take the shape shown. In many industrial meters the greater the rate of flow the less the per cent slip. The percentage of slip at low rates increases very rapidly in most meters. The region where this occurs is known to those in the meter industry as the region of slip, and is indicated by the upward deflection of the proof line at low rates of flow. The actual test curve is above the displacement curve, because of slippage as shown. To compensate for this slippage, the meter manufacturers provide for change gears in the gear train to the meter index. These gears are intended to take care of the slip and give an average index reading which is correct throughout the operative range of the meter.

Design Requirements

In view of what has been said, it would appear that the design requirements of a meter, in regard to accuracy of registration requirements only, would be quite simple. The first requirement is that the meter must be constructed in such a way that it offers little resistance to flow. Since pressure loss in pipe lines is an important factor, it should not be increased appreciably by placing meters with high pressure loss in the line, as this would mean a considerable increase in the pumping cost. Also, if the meter has a high pressure loss, there is a possibility of absorbed gases in the oil being driven off, in which case the accuracy of measurement would be affected. On the other hand, in a light-running meter, the register load may be the greater portion of the load on the metering element, and a slight change in the friction load in the register due to dust, corrosion, lubrication failure, and the like may cause the light-running meter to change calibration sharply.

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[1] Professor of Mechanical Engineering, The Pennsylvania State College. Mem. ASME.

[2] "Results of Tests on Volumeters for Liquid Hydrocarbons," by R. J. S. Pigott, E. E. Ambrosius, and E. W. Jacobson, Trans. ASME, vol. 65, 1943, pp. 350–352.

Contributed by the Research Committee on Fluid Meters and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-171.

This will apply to a higher absorption meter to a lesser degree. Another consideration is that all factors which enter into slip must combine in such a way that slip, for any set of fluid conditions, will be proportional to the actual flow rate through the meter. This latter condition will give a meter of constant per cent error, and it will be possible to install a gear train that will make the proof line coincide with the displacement according to register.

To determine the slip of any meter it is necessary to know the true displacement of the meter in question. The displacement of any meter can be determined by means of a setup as shown in the schematic diagram, Fig. 2. The basic idea in this setup is to drive the meter at a very low rate of flow, under such conditions that the differential pressure across the meter is zero. Under these conditions it is assumed that the slip is zero, and the volume of liquid passed, divided by the number of corresponding displacements, will give the unit displacement.

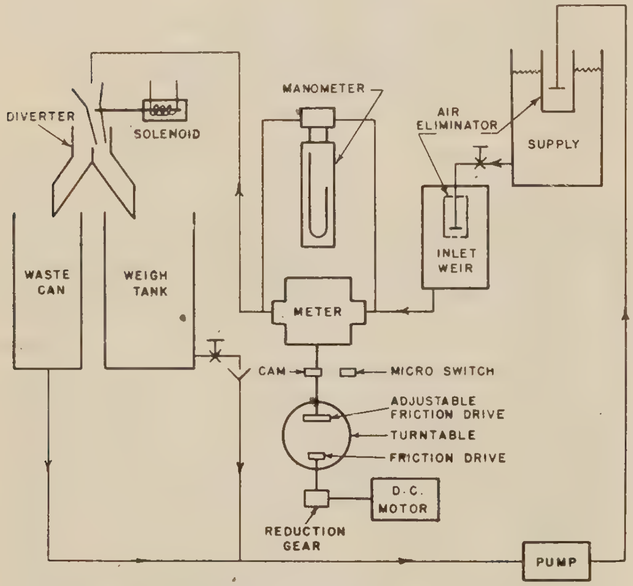

Fig. 2 Schematic Diagram of Test Setup for Determining Displacement of Meters

One of the important features of this setup must be the assurance of air elimination. This can be accomplished by use of a sharp-edged overflow in the supply tank and in the inlet weir. In this manner the fluid is prevented from trapping air and carrying it along in suspension. All possible points of splashing in the weigh tank, waste can, etc., that may lead to entrapment of air are reduced to a minimum by installation of antisplash racks. This is done because the best step in the solution of the air-elimination problem is to prevent the air from entering the fluid in the first place.

A variable-speed direct-current, motor-driven reduction unit is used to give constant rotation to the meter. By means of a line rheostat and the friction-drive wheel, it is possible to obtain speeds as low as 1 rpm in either direction. A cam located on the final drive shaft will close the microswitch at the same point each revolution. Closing this switch energizes the counter at each revolution, as well as the diverter solenoid at the beginning and end of each test run.

The inlet weir should be so constructed and placed that it can be raised and lowered. By so doing and by adjusting the valve on the meter-supply tank the differential pressure across the meter readily can be held at a zero value.

When the displacement determinations were made on the meter in question, equipment similar to that shown was used, and consistent checks were obtained. For example, seven tests indicated an average displacement of 1.9765 gal per revolution, with a maximum deviation of only 0.07 per cent from the average.

Results

The graphical and tabulated results given in this paper represent only average values for one meter. This was done by plotting all test data and then making the best estimate possible for the average curves representing these test values. To minimize the data included, results taken from these average curves are given for even increments of flow. Since the meter which these data represent had a maximum rating of 300 gpm, no values are given for less than 50 gpm; the basis for this being that the upper 85 per cent of the capacity of a meter is considered its operating range.

Pressure Loss and Flow Relation. In order to make an analysis of the pressure drop across a meter, a study should be made of the controlling factors. In Fig. 3 is plotted, at constant viscosity and temperature, the relation of pressure loss (inches of water) against the actual flow rate (gallons per minute). In these tests the oil as well as the temperature of each was changed, in order to increase the range of viscosity. From these curves it may be observed that pressure drop is a function of both rate of flow and absolute viscosity of the oil. As may be seen from Fig. 3, representing the 84 F tests, for any given flow rate the pressure loss is proportional to viscosity. If, however, the viscosity is decreased sufficiently, a point is reached where the pressure loss becomes independent of the viscosity. This condition holds only if the character of the fluid being measured remains approximately the same. If the viscosity is decreased to a point where the lubrication is lost, the pressure loss may actually increase and the error curve rises. This is apparent in Fig. 3 where the pressure drop, when using gasoline is shown to be almost as great as in the case of the thin oil. In Fig. 5 the values for error are given for gasoline and therefore may be compared with those for

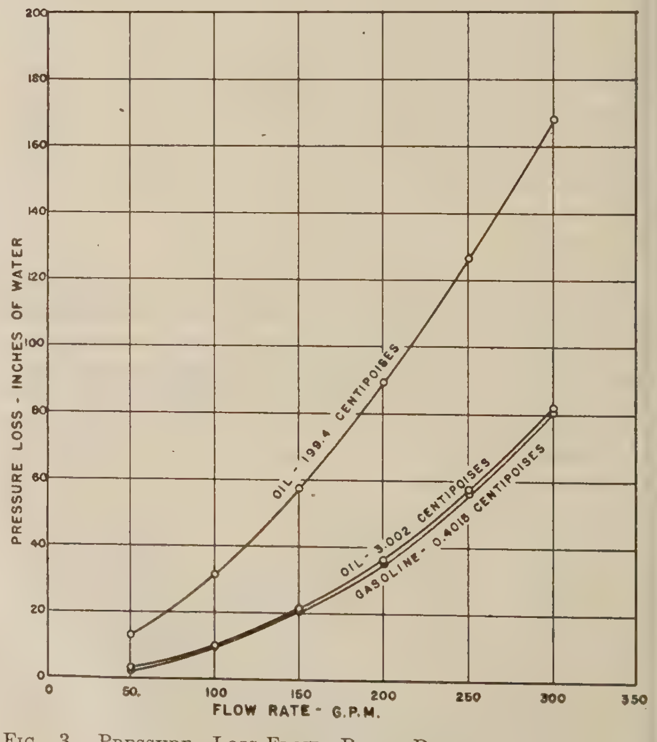

Fig. 3 Pressure Loss-Flow Rate Relations for Three Different Liquid Hydrocarbons, All at 84 F

the other oils. The lack of lubricity in the case of the gasoline and its effect upon the performace of the meter became apparent.

Slip Relations. From the expermentally determined displacement of 1.9765 gal per cycle and the gear ratio of the meter, which showed 2 gal on the meter index for each cycle or revolution of the meter element, the slip could be determined for any meter reading. The slip for even increments of flow is determined by correcting the meter-register reading to that of displacement. The difference between the true or measured volume passing through the meter and the displacement during the same time interval is known as slip, and is plotted in Fig. 4. It will be noted that the slip does not increase in a linear relation with flow rate. This observation means that this meter, under these conditions, will not have a constant per cent error over the entire flow range. This fact will be noted in a later figure.

By reversing the calculations in obtaining the slip, shown in Fig. 4, values of slip at regular intervals of flow could be converted to equivalent register readings. Thus the ratio V_a/V_m could be calculated at these same regular intervals, where V_a is the actual volume passing through the meter and V_m is the corresponding meter indication. The meter error, $(V_a/V_m—1)$, is plotted against flow rate in Fig. 5. When the meter error has a plus value, it signifies that the actual flow through the meter is greater than indicated while the reverse is true for negative values. The numerical values of temperature, viscosity, pressure loss, and error used in plotting Figs. 3 and 5 are given in Table 1.

In Fig. 5 it will be noted that at low rates of flow, the slip, when using gasoline, is no greater than that for the heavy oil. This can be attributed to the corresponding relatively low pressure drop. However, as the flow rate increases, the slip increases at a more rapid rate, owing to a combination of increased pressure loss and the low viscosity of the gasoline, which is a naturally poor sealing fluid.

Curves in Fig. 6 and 7 were drawn from values taken from Table 2. At constant temperature, pressure loss was plotted against viscosity in Fig. 6, and error against viscosity in Fig. 7. From Fig. 6 it will be noted that at all flow rates the pressure loss increases as the viscosity increases. At low rates, the viscosity has little effect upon the pressure loss, while at high flow rates the pressure loss increases sharply with the increase in viscosity. In Fig. 7 it will be observed that the error in all cases decreases at constant flow rate with an increase in viscosity. This is a natural

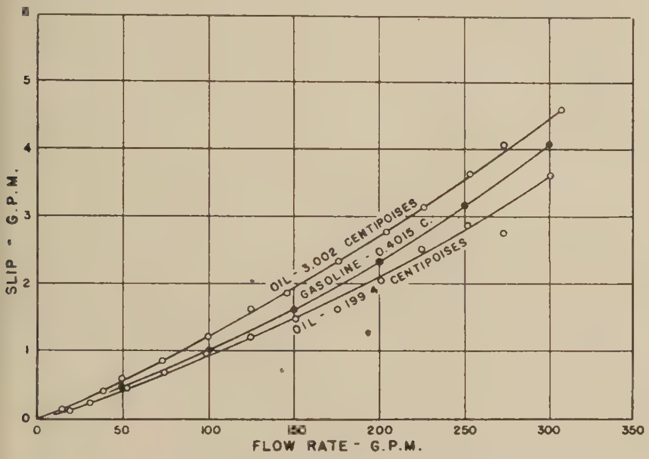

FIG. 4 SLIP-FLOW RATE RELATION FOR THREE DIFFERENT LIQUID HYDROCARBONS, ALL AT 84 F

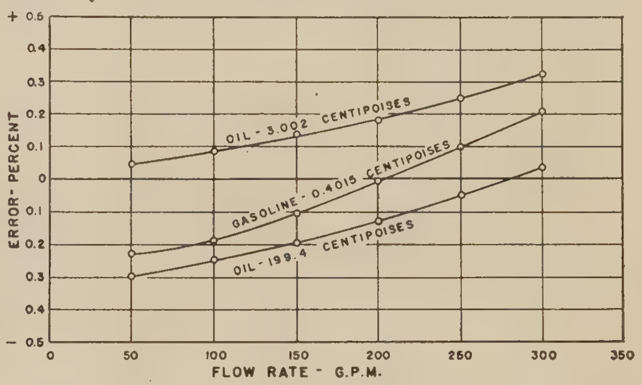

FIG. 5 ERROR-FLOW RATE RELATION FOR THREE DIFFERENT LIQUID HYDROCARBONS, ALL AT 84 F

TABLE 1 VALUES FROM AVERAGE CURVES

Viscosity, centipoises	Temp, deg F		Flow, gpm					
			50	100	150	200	250	300
1.177	176.5	P	5.0	13.5	24.5	39.2	58.5	81.0
		E	—0.550	—0.478	—0.412	—0.350	—0.290	—0.235
		S	0.315	0.690	1.145	1.650	2.220	2.830
17.22	176.5	P	6.5	16.2	30.5	49.0	71.0	100.5
		E	—0.065	0.1266	0.1605	0.1368	0.0455	0.0489
		S	0.520	1.300	2.000	2.620	3.050	3.380
1.935	123.5	P	3.0	9.5	20.0	35.5	55.5	80.0
		E	—0.295	—0.205	—0.125	—0.055	0 015	0.078
		S	0.430	0.970	1.580	2.210	2.925	3.740
56.19	123.5	P	8.0	19.5	37.5	60.8	88.5	118.0
		E	—0.095	—0.020	0.050	0.108	0.162	0.210
		S	0.540	1.170	1.860	2.560	3.330	4.156
2.375	105.0	P	3.2	9.5	20.0	35.5	56.5	79.5
		E	—0.036	0.005	0.045	0.095	0.153	0.225
		S	0.570	1.180	1.840	2.530	3.310	4.200
95.51	105.0	P	8.5	22.5	43.0	68.0	99.0	132.0
		E	—0.060	—0.038	—0.015	0.010	0.042	0.075
		S	0.560	1.140	1.740	2.370	3.040	3.750
3.002	84.0	P	3.0	10.0	21.5	36.5	57.5	82.0
		E	0.048	0.085	0.132	0.185	0.246	0.320
		S	0.610	1.260	1.970	2.710	3.550	4.480
199.4	84.0	P	13.0	31.5	57.5	89.5	126.5	168.0
		E	—0.298	—0.250	—0.192	—0.128	—0.052	0.035
		S	0.440	0.930	1.470	2.100	2.320	3.630
0.0	84.0	P	2.6	9.7	21.0	35.6	56.3	80.4
			VALUES FOR GASOLINE					
0.4015	84.0	P	4.0	10.12	22.25	37.75	58.10	82.6
		E	—0.2271	—0.1869	—0.1028	—0.0051	0.0983	0.2011
		S	0.475	0.990	1.610	2.340	3.180	4.1200

NOTE: P = Pressure loss, in. of water
E = Error, per cent
S = Slip, gallons per minute

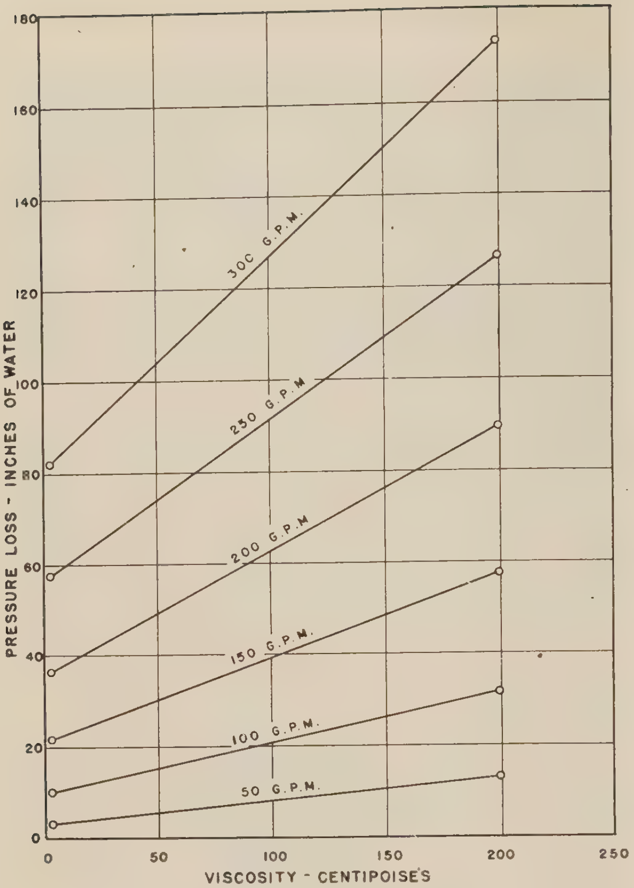

Fig. 6 Pressure-Loss Viscosity Relation for Even Increments of Flow Rate, All at 84 F

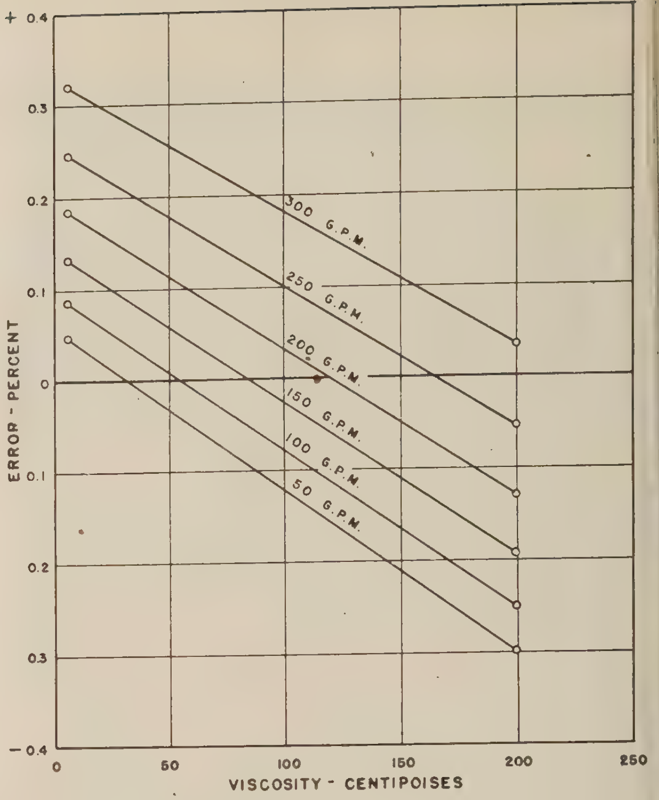

Fig. 7 Error-Viscosity Relation for Even Increments of Flow Rate, All at 84 F

phenomenon since the heavier oils seal better than the light. It will also be noted that the error increases quite rapidly at constant viscosity with an increase in flow rate. This phenomenon

TABLE 2 VALUES FROM PRESSURE LOSS VERSUS FLOW, AND ERROR VERSUS FLOW CURVES

Viscosity, centipoises	Flow, gpm	84 F		105 F		123.5		176.5 F	
		PL[a]	Error	PL	Error	PL	Error	PL	Error
3	50	3.0	0.046	2.9	—0.038	3.0	—0.293	5.2	—0.479
	100	10.0	0.086	9.2	0.004	9.6	—0.203	13.8	—0.418
	150	21.5	0.140	20.0	0.043	20.25	—0.123	25.1	—0.350
	200	36.5	0.182	35.4	0.093	35.9	—0.053	40.3	—0.300
	250	57.5	0.249	57.0	0.153	56.0	0.018	60.0	—0.254
	300	82.0	0.323	79.4	0.224	80.7	0.080	82.5	—0.215
10	50	3.1	0.031	3.0	—0.040	3.6	—0.268	5.9	—0.212
	100	10.2	0.072	10.1	0.000	10.9	—0.179	15.0	—0.151
	150	22.6	0.127	21.9	0.040	22.4	—0.100	27.8	—0.100
	200	38.7	0.171	38.0	0.088	39.1	—0.032	44.6	—0.086
	250	59.9	0.238	59.9	0.145	60.2	0.037	65.3	—0.108
	300	84.8	0.313	83.2	0.212	85.5	0.096	91.6	—0.132
30	50	4.1	—0.004	4.2	—0.045	5.4	—0.195	7.6	0.550
	100	13.0	0.039	13.2	—0.008	14.6	—0.111	18.25	0.610
	150	26.1	0.093	26.8	0.026	29.0	—0.036	35.3	0.621
	200	43.8	0.140	45.0	0.069	48.4	0.028	56.7	0.525
	250	66.9	0.208	69.1	0.120	72.5	0.090	81.0	0.308
	300	93.5	0.283	94.9	0.180	99.6	0.143	116.0	0.101
60	50	5.5	—0.056	6.2	—0.052	8.2	—0.083	...	...
	100	16.1	—0.012	17.3	—0.022	20.0	—0.007	...	...
	150	31.9	0.042	34.2	0.007	38.8	0.061	...	...
	200	52.0	0.092	55.2	0.041	62.5	0.119	...	...
	250	77.2	0.163	82.8	0.083	90.9	0.172	...	...
	300	106.9	0.238	112.0	0.132	120.5	0.219	...	...
100	50	7.3	—0.124	9.2	—0.062	...	...	...	...
	100	20.5	—0.079	23.2	—0.041	...	...	...	...
	150	39.1	—0.026	44.0	—0.019	...	...	...	...
	200	62.8	0.028	69.5	0.005	...	...	...	...
	250	91.2	0.102	100.8	0.035	...	...	...	...
	300	124.6	0.180	134.5	0.068	...	...	...	...
150	50	10.1	—0.210	...	...	...	...	...	...
	100	26.0	—0.163	...	...	...	...	...	...
	150	48.0	—0.112	...	...	...	...	...	...
	200	76.1	—0.051	...	...	...	...	...	...
	250	109.1	0.027	...	...	...	...	...	...
	300	146.3	0.105	...	...	...	...	...	...
200	50	13.0	—0.297	..	...	...	...	...	...
	100	31.8	—0.246	...	...	...	...	...	...
	150	57.8	—0.196	...	...	...	...	...	...
	200	89.9	—0.128	...	...	...	...	...	...
	250	127.2	—0.046	...	...	...	...	...	...
	300	168.8	0.033	...	...	...	...	...	...

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[a] Pressure loss, in. of water.

is associated with pressure drop, which, as has already been shown in Fig. 3, increases exponentially with flow rate at constant viscosity and temperature.

Pressure Loss at Zero Viscosity

As previously stated, the pressure drop is made up of the work required to drive the meter mechanism, including the register, dissipation of energy due to fluid friction, turbulence, and the change of direction of the fluid flow. If a fluid of zero viscosity were to be used, all of the loss due to fluid friction and part of that due to turbulence would reduce to zero. The effect of this may be represented by extending the lines in Fig. 6 to the left until they intersect the zero line of the abscissa scale. The intercept on the pressure-drop scale represents the sum of all mechanical losses. By plotting the mechanical losses as taken from the zero intersection and plotting them as meter losses at zero viscosity, Fig. 8 was drawn. For simplicity, this figure shows only a condition of constant temperature and viscosity. The oil used had a condition of 84 F and a viscosity of 199.4 centipoises. It will be noted that at full meter capacity the mechanical losses and fluid losses are about the same. On the basis of this figure it will be noted that the losses due to mechanical friction follow the generally accepted square law. Or, stating it in another way, if the rate of flow is doubled, the mechanical friction losses will increase 4 times. The figure shows that the pressure loss due to fluid friction increases almost linearly with flow rate, in spite of the fact that the pressure loss was measured over the entire meter, where, unquestionably, turbulence existed. This would suggest that the laws of fluid mechanics could be applied readily. This was done in a few cases, using assumed areas of the slip passages, with fairly consistent checks against experimentally determined slip. The checks were better at the upper half of the flow range. There may be some basis for this, inasmuch as the pressure loss due to the fluid is almost exactly proportional to the flow rate in this region, Also, the experimental results indicate an almost exact linear relation between slip and pressure drop over this region. The calculations are not included in this paper since the meter was not torn down during the test in order to obtain its exact dimensions.

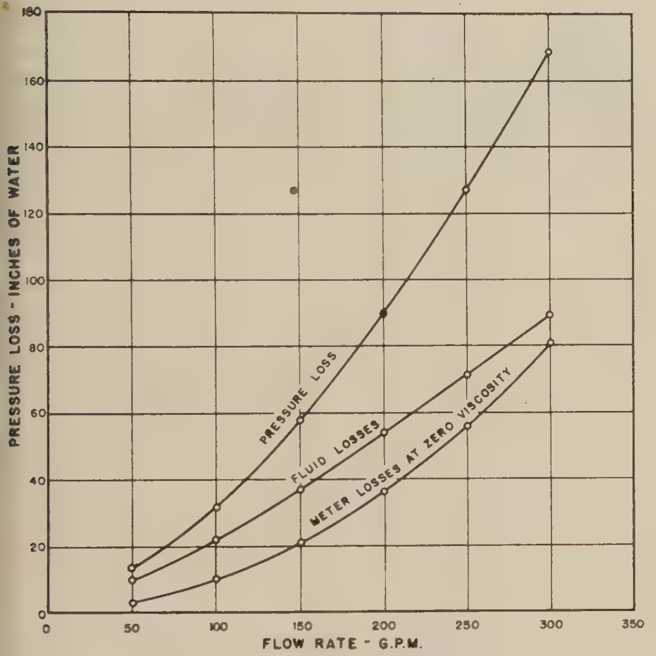

Fig. 8 Pressure Loss-Flow Rate Relation at 84 F, and Oil at 199.4 Centipoises

By breaking down the pressure loss in this manner, the effects of streamlining and polishing the internal passages of the meter, in order that the oil may pass through with as little agitation and disturbance as possible, can be studied. Also, the mechanical friction in both the metering element and register could be studied from such data in order to keep them as low as possible, or better still, give them values such that slip will approach the ideal, namely, proportional to flow. When studying the combination of error and pressure-loss curves, it will be noted that this meter has fairly good sealing and pressure-loss characteristics. Its total spread of error for any given viscosity at 84 F, Fig. 5, is only about 0.3 per cent.

In general, it may be stated that if a meter has a combination of poor sealing and high pressure loss, it will have a rising error curve at higher flow rates. In view of this, the error at the higher flow rates could be reduced somewhat by reducing the pressure loss. This can be accomplished by reducing mechanical friction, or by streamlining and reducing turbulence. It could also be accomplished by reducing the clearances, thereby improving the sealing characteristics. The data indicate for oil of 10 centipoises viscosity or less, that, as the temperature was increased, the sealing characteristics improved. This was brought about by a greater change in the expansion of the metering element as compared to the meter case with temperature; the meter element

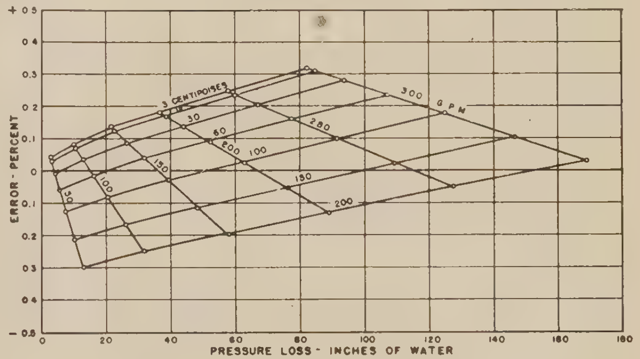

Fig. 9 Error-Pressure Loss Relations, All Test Points, at 84 F

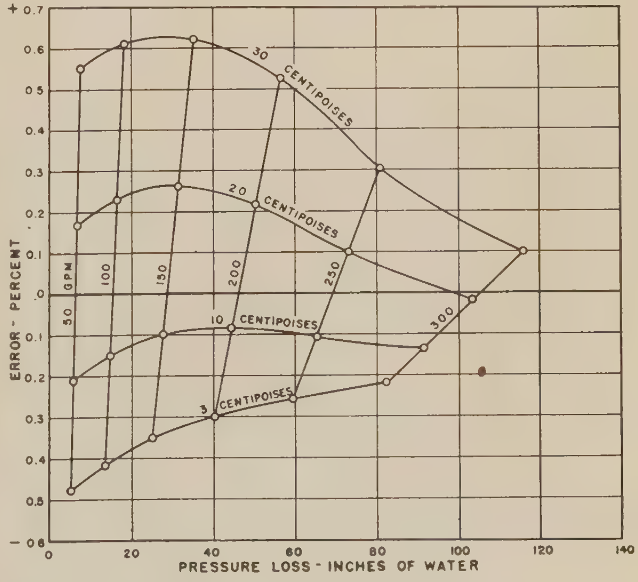

Fig. 10 Error-Pressure Loss Relations, All Test Points at 176.5 F

being an aluminum-copper alloy, while the case was cast iron. Temperature has an effect that is difficult to evaluate since it is dependent upon clearances, types of material used, ambient temperature, and inherent design features.

Error Characteristics. Meter error as a function of pressure loss is shown in Figs. 9 and 10. In Fig. 9 it covers a constant condition of 84 F temperature, and in Fig. 10, 176.5 F. In both figures the points of constant viscosity and flow rate are connected in order to complete the pattern of the meter characteristics. A general reversal of characteristics will be noted between the two conditions. For instance, at 84 F, at constant flow rate, as the viscosity increases the pressure loss increases and the per cent error decreases, while at 176.5 F, at constant flow rate the pressure loss increases, the viscosity increases, and the per cent error increases. It should be observed, however, that the range of viscosity on the 176.5 F curves is quite small compared to the 84 F curves. This reversal can be attributed to the increased pressure loss at the elevated temperature. At 84 F, and at constant flow rate, the viscous effects predominate, and the meter will seal better with the higher viscosity oil. At the elevated temperature this condition is no longer true. Here the pressure drop is sufficient to overcome the neutralizing effect of viscosity, and slip actually increases with an increase in viscosity at constant rate of flow.

From the data given in Table 2 it will be noted that when the intermediate temperatures of 105 and 123.5 F are considered, this reversal of characteristics is gradual and definitely systematic.

CONCLUSIONS

The work reported in this paper hints that it may be possible eventually to predict the performance of a particular displacement-meter design by careful and complete testing. Such tests would lead ultimately to an improvement in the design and general performance.

The data presented show that, with further study and testing of like designs, combinations of factors might be found which would compensate for the deleterious effects of others and thus make the meter perform in a more uniformly good manner.

ACKNOWLEDGMENT

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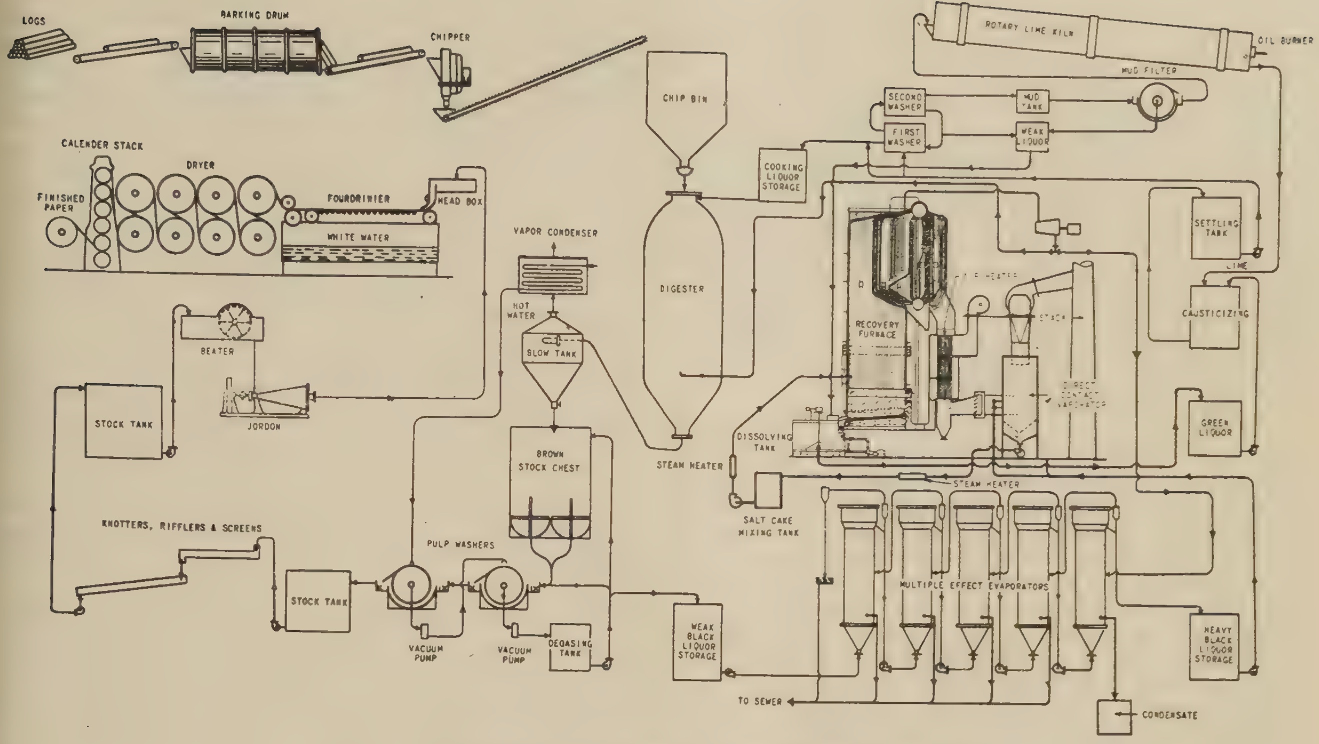

Fig. 1 Diagrammatic Flow Sheet of Typical Kraft Paper Mill

Developments in Kraft-Process Recovery-Unit Design and Performance

By R. K. Allen,[1] New York, N. Y.

Recent developments in design of Kraft-process recovery units, utilizing the Tomlinson method of combustion, are described. The comparative performance is given of early and recent types of Tomlinson recovery units. Economic factors affecting the selection of recovery-system equipment are included.

The application of steam-generating equipment in pulp mills, utilizing the B&W-Tomlinson method for the combustion of black liquor from the Kraft pulping process, has been described in previous papers by Wilcoxson and Ely in 1937 and 1940.[2,3] Although the B&W-Tomlinson method of combustion has been retained, the many changes made in design since then have affected recovery-unit performance materially. It is the purpose of this paper to describe the principal design changes, the reasons for them and their effect on recovery-unit performance.

Kraft Pulping Process

A flow sheet for a typical Kraft mill is shown in Fig. 1. The logs entering the mill are first barked, chipped, and then charged into a digester, where they are cooked under pressure with steam, using a solution of sodium hydroxide and sodium sulphide known as the "cooking liquor." In the cooking operation the lignin binder holding the cellulose fibers of the wood together is dissolved.

After cooking, the cellulose fibers now called "pulp" are separated from the spent cooking liquor in the pulp washers. The pulp then goes through several refining processes and to the paper machine.

The spent cooking liquor with the included dissolved lignins from the wood is called "black liquor." As the black liquor comes from the washers, it is quite dilute and has a heating value barely sufficient to evaporate its water content.

The black liquor is concentrated first in multiple-effect evaporators, using steam. It then goes to the recovery unit where it is further concentrated in a direct-contact evaporator, using the sensible heat in the flue gas from the recovery unit.

After the addition of sodium sulphate in the mixing tank to make up for chemical losses in the system, the black liquor is

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[1] Staff Engineer, The Babcock & Wilcox Company. Jun. ASME.

[2] "Burning of Waste Liquors in the Kraft and Soda-Paper Industries," by L. S. Wilcoxson, Trans. ASME, vol. 60, 1938, pp. 25–31.

[3] "Recovery-Unit Performance in Burning Kraft Process Black Liquor," by F. G. Ely and L. S. Wilcoxson, *Paper Trade Journal*, vol. 110, May 9, 1940, pp. 30–36.

Contributed by the Fuels Division and presented at the Spring Meeting, New Orleans, La., March 1–4, 1948, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 48—S-2.

burned in the recovery furnace. In the B&W-Tomlinson method of combustion the concentrated black liquor is sprayed upon the furnace walls for dehydration prior to final combustion of the dried char on the furnace hearth.

In the recovery furnace, heat from the combustion of the organic liquor constitutents is obtained and, more important, the spent sodium salts in the liquor are recovered as smelt. Another essential function of the furnace is the reduction of the sodium-sulphate content of the black liquor to sodium sulphide.

The smelt, composed largely of sodium carbonate and sodium sulphide, is dissolved in water in the dissolving tank to form green liquor.

The green liquor is subjected to a causticizing treatment to convert the sodium carbonate to hydroxide. The liquor is then ready for use again as cooking liquor in the digester.

Increase in Capacity

One of the most important reasons for the changes made in the design of recovery units during the last 10 years has been the continuing scarcity and high cost of labor, which has made improvement in design necessary in order to reduce operating-personnel requirements. Many of the changes have been made possible by technological improvements, and others have been made as dictated by operating experience with earlier installations.

Perhaps the most apparent change in recovery-unit design has been the increase in capacity of individual recovery units. This has permitted a reduction in the number of operating personnel because of the fewer number of recovery units required for a given mill capacity. Increase in recovery-unit capacity has also reduced the relative over-all installation costs because of the reduced space and building requirements, in addition to the reduced cost per ton of capacity of larger-size recovery units.

In 1937 the largest B&W-Tomlinson recovery unit installed had a capacity of 130 ton/day.[4] Today, units with capacities up to 275 ton/day are in operation and two 350 ton/day capacity units are under construction. This is nearly 3 times the capacity of the largest unit of 10 years ago.

A typical 125 ton/day unit, installed in 1937, is shown in Fig. 2. This unit has a separate furnace connected to a three-drum waste-heat-type boiler by a water-cooled flue. The concentrated black liquor is sprayed on the side and rear walls of the furnace through an oscillating spray nozzle located in the front wall. The liquor, dehydrated on the walls, falls to the furnace hearth as a char and is burned. To obtain reduction of the sodium sulphate in the char to sodium sulphide and to maintain a low fuel-bed temperature, the char is burned in a reducing atmosphere obtained by supplying a deficiency of air for complete combustion to the fuel bed through primary-air ports located close to the furnace floor. Air to complete combustion is admitted through secondary-air ports higher in the furnace.

Even at the minimum temperature at which stable ignition of the char can be maintained, there is some sublimation of sodium salts from the fuel bed. These vaporized salts are carried from the furnace with the flue gases. As the gases are cooled in passing through the boiler, superheater, and air heater, the sublimed salts deposit out on the heat-absorbing surfaces.

In addition to the sublimed chemical, black-liquor particles with their included sodium salts are entrained mechanically in the furnace gases. These particles adhere to the heating surfaces on contact.

The chemical deposits on the heating surfaces from the sublimed chemicals and the mechanical entrainment of black-liquor particles create a difficult cleaning problem, and in earlier-type units such as shown in Fig. 2, considerable hand-lancing was required to keep the boiler, superheater, and air-heater gas passes open.

A 275 ton/day capacity unit of a newer design, similar to that shown in Fig. 3, was placed in operation in 1946. This unit employs a large completely water-cooled furnace similar to many large central-station power boilers. For protection, the tubes in the smelt zone in the lower portion of the furnace walls and the furnace floor are covered with chrome-ore refractory, anchored to the tubes by pin studs welded to the exposed face and sides of the tubes. The upper portion of the furnace walls and the boiler walls back as far as the rear of the superheater employ a bare-tube flat-stud construction for maximum heat transfer. The studs are welded to the sides of the tubes to form a continuous bare-metal wall surface.

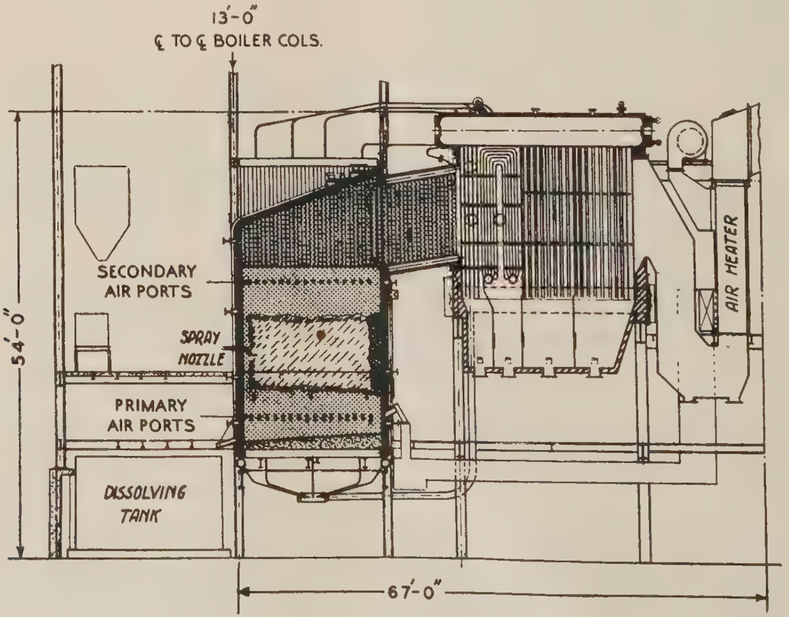

Fig. 2 Three-Drum Recovery Unit Installed in 1937; Capacity 125 Tons per Day

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[4] Recovery-unit capacity, expressed as "ton/day," is equivalent to burning the black liquor obtained from this tonnage of pulp production per day and assumes that 3000 lb of black-liquor solids are obtained per ton of pulp produced.

Both the boiler and economizer are vertical-tube two-drum types. A tubular gas-air heater, employing parallel flow of gas and air, is included in this particular installation. The gas flows through the inside of the tubes and the air flows over the outside of the tubes, making three passes, crossflow.

The relative physical sizes of the two units, shown in Figs. 2 and 3, can be compared by means of the over-all dimensions shown.

Reduction In Cleaning Requirements

A reduction in the man-power requirements for operation has been made possible by changing the arrangement of the convection-heat-absorbing surfaces, particularly the boiler screen and superheater, so that the resulting gas temperature and flow conditions substantially reduce the deposition of chemical solids and facilitate the removal of the solids that are deposited. In the past the cleaning problem has been most severe in the boiler-screen and superheater sections, and the present design provides a more uniform and lower gas temperature across the tubes in these sections.

In general, the chemical deposits on the heating surface in the high-temperature gas zones are hardest, and consequently most difficult to remove. As the gas temperature drops through the unit, the deposits become softer until in the relatively cool zones they appear as a very fine adhesive powder.

A study of actual temperature and velocity conditions obtained by test traverse ahead of the superheater on a 275 ton/day capacity unit, similar to the one shown in Fig. 3, is given in Fig. 4. During the time the traverse was made, the unit was being operated at a rating of 273 ton/day with a liquor-firing concentration of 67 per cent solids. The values given are the averages of temperatures and velocities taken at seven points across the width of the unit at each elevation shown.

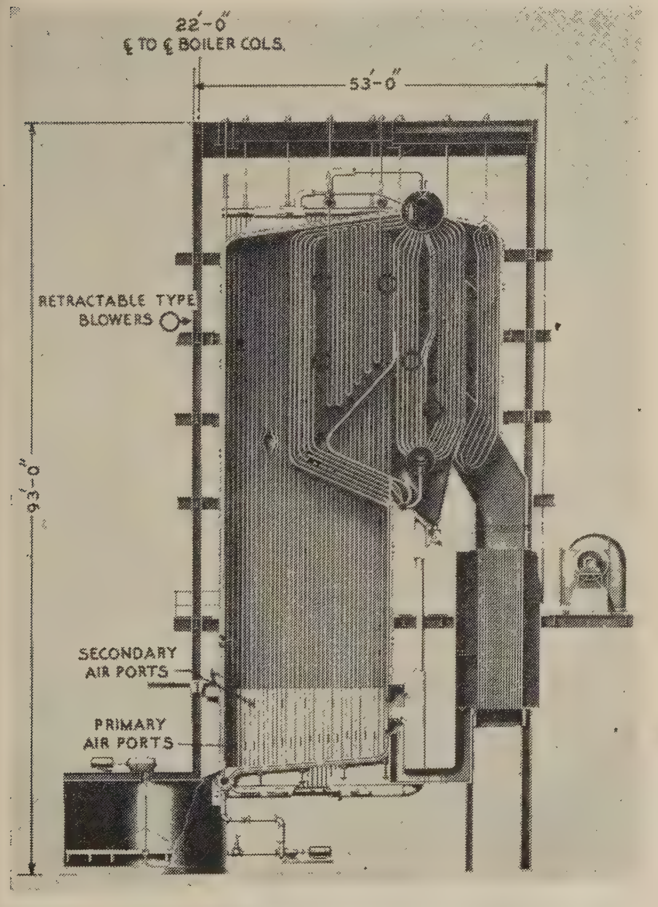

Fig. 3 Two-Drum Recovery Unit; 275-Ton per Day Capacity; Installed 1946

The gas velocities and flow paths, determined by Pitot-tube readings, are indicated by vectors on the figure. Temperature measurements, obtained with high-velocity platinum versus platinum-rhodium thermocouples, are indicated numerically. Other traverses taken at different ratings and liquor-firing concentrations showed temperature and velocity patterns consistent with this example.

The average gas temperature entering the superheater is 1465 F for the traverse shown. The high-velocity thermocouples used on these tests will give temperature values approximately 100 deg F higher than would be obtained with bare thermocouples. This is due to the cooling of the bare thermocouple below the gas temperature by radiation from the couple to the adjacent relatively cold boiler and superheater surfaces. A high-velocity thermocouple will indicate the true gas temperature, and a bare thermocouple will indicate the approximate temperature of a solid particle entrained in the flue gases. Because the difference in gas temperature indicated by the two methods is large, temperature data from different sources can be directly compared only when taken by, or corrected to, the same method of measurement.

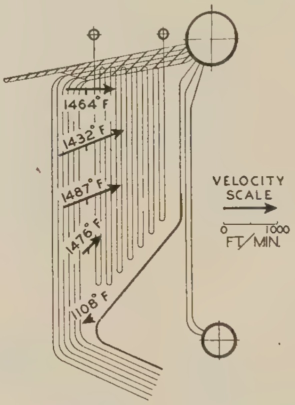

Fig. 4 Gas Velocities and Temperatures Entering Superheater

As indicated in Fig. 4, a relatively uniform temperature and velocity distribution is obtained over the height of the superheater, except for a zone just above the superheater floor where reverse gas flow and low gas temperature occur. The boiler-screen and superheater tubes are arranged so that any hard chemical deposits removed from them are returned to the furnace, melted, and discharged through the tap hole as smelt. This avoids the difficult problem of handling hard deposits from the boiler hoppers. The relatively low gas temperature and reverse flow above the superheater floor assists the return of deposits to the furnace.

This distinctive and favorable pattern of velocity and temperature is due to the furnace gases being directed toward the front of the furnace by the rear furnace arch and also due to the large stack effect produced in the relatively high furnace. This stack effect causes the hottest furnace gases to rise to the top of the furnace before entering the boiler screen. The hottest gases thus exposed to the entire furnace surface are cooled a maximum amount. Because of the forward direction of the furnace gases and the stack effect, the static pressure at the bottom of the boiler screen is lower than that at the top. With the low resistance to gas flow through the screen and superheater, the difference in static pressure between the top and bottom of the boiler screen is sufficient to induce a slight reverse flow of relatively cool gases back along the superheater floor and into the furnace. These recirculated gases mix with the high-temperature gases in the upper part of the furnace to reduce the average temperature of the gases entering the boiler screen.

The chemical deposits collecting on the boiler screen and superheater have been found to have a fusion temperature ranging from 1500 F to 1650 F. In order to avoid a difficult cleaning job and the possibility of sulphur attack on the superheater tubes and tube spacers, it is obviously desirable to maintain the gas temperature entering the superheater below the fusion temperature of the deposits. With even temperature distribution to the superheater, it is possible to have the average temperature entering the superheater close to the fusion temperature without the possibility of local smelting which might otherwise occur due to temperature unbalance. The nose baffle under the superheater shields the superheater from radiation from the hot lower portion of the furnace and avoids elevating the temperature of the chemical deposits above that of the surrounding gas.

Burning black-liquor char particles, which may be mechanically entrained in the furnace gases, contain sufficient combustible content to melt the ash included in the char. These burning char particles tend to stick to the tubes of the boiler screen and superheater and produce hard smelt deposits, even though the surrounding gas is at a temperature below the fusion point of the deposits.

Smelt deposits on boiler heating surfaces from this source have been further minimized by reducing the quantity of unburned char particles adhering to the boiler screen and superheater. This reduction has been obtained by lowering the ports for admission of secondary air, necessary for completion of combustion, to just above the fuel bed. This gives a maximum time to burn out the combustible matter in the char particles entrained in the furnace gases. The present lower elevation of the secondary-air ports can be seen from a comparison, Fig. 2 and Fig. 3.

The elevation of the primary-air ports just above the furnace floor has been retained. The quantity of combustion air admitted through the primary-air ports to the fuel bed is kept as low as possible consistent with maintaining stable ignition and the free flow of smelt, the amount generally being about 65 per cent of the theoretical combustion-air requirement. Operating with a minimum primary-air quantity results in less mechanical entrainment of char particles in the furnace gases and helps to reduce the quantity of char particles adhering to the heat-absorbing surfaces.

In the cooler gas zones of the boiler and economizer of the earlier designs, it has been found that the chemical deposits tend to pack and are more difficult to remove at points where the gas velocity and turbulence are highest. In the newer designs it has been possible to ease the cleaning problem in the cooler zones by modification in arrangement of the heating surface and by reducing the flue-gas weight per ton of capacity. The reduction in gas weight has been obtained by reducing the air infiltration to the boiler setting. This has been accomplished by improving the boiler-setting design while retaining an ample number of doors for inspection, access, and lancing. The lance-port arrangement and steel-clad monolithic wall construction used in the boiler walls are shown in Fig. 5.

Operation with a lower excess air at the outlet of the unit has resulted in an increase in thermal efficiency and a reduction in load on subsequent equipment such as the induced-draft fan and precipitator.

Table 1 gives a comparison of the actual performance of the unit shown in Fig. 2, and the newer 275 ton/day capacity unit similar to that shown in Fig. 3. In addition to general operating information, the data include gas temperatures and per cent of theoretical combustion air in the flue gas throughout the units. Liquor analyses, chemical loss, and heat balances are also given.

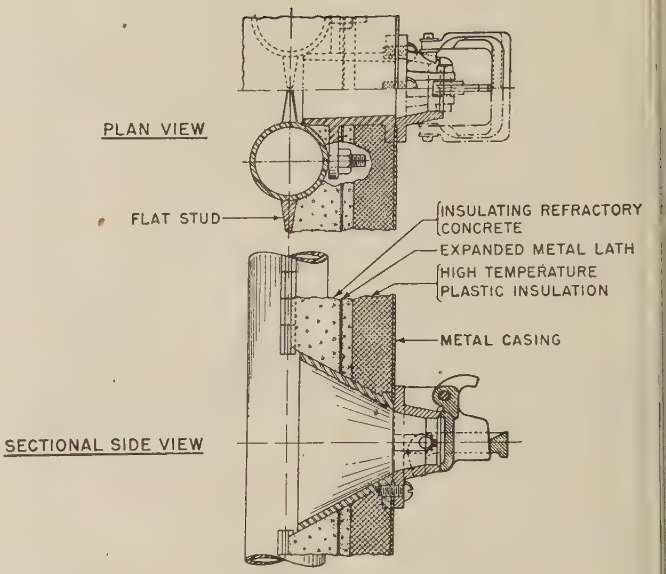

FIG. 5 LANCE-PORT AND WALL CONSTRUCTION

TABLE 1 COMPARISON OF PERFORMANCE OF 125 TON/DAY AND 275 TON/DAY CAPACITY RECOVERY UNITS

Test duration, hr	9.5	8.0
Boiler	Fig. 2	Fig. 3
Rating, tons/day, design	125	275
Rating, tons/day, actual during test	127	273
Steam output during test, lb per hr	50520	114731
Steam pressure, superheater outlet, psi	457	454
Steam temperature, superheater outlet, deg F	690	680
Feedwater temperature, deg F	307	275
Air temperature leaving air heater, deg F	358	343
Heat of reduction of Na_2SO_4, per cent	5.5	2.6
Heat in smelt leaving furnace, per cent	3.8	4.5
Latent heat loss; fuel moisture and H_2, per cent	18.9	16.3
Sensible heat in stack gases, per cent	7.2	7.1
Evaporation in spray tower, per cent	9.2	4.4
Heat absorbed by steam, per cent	54.5	59.4
Unburned combustible loss, per cent	0.8	0.1
Radiation and unaccounted for, per cent	0.1	5.6
Total	100.0	100.0
Black liquor fired, lb per hr	29110	57270
Concentration of black liquor as fired, per cent solids	54.7	59.6
Salt cake fed (as Na_2SO_4), lb per hr	2040	1980
Analysis of black liquor as fired:		
Carbon, per cent	18.65	20.7
Hydrogen, per cent	1.95	2.0
Oxygen + nitrogen, per cent	5.25	4.8
Sulphur, per cent	2.40	2.5
Ash, per cent	26.45	29.6
Moist, per cent	45.30	40.4
Heating value as fired, Btu per lb	3372	3660
Total soda loss in flue gas leaving air heater (as Na_2SO_4), lb per ton	137.5	135
Green liquor reduction, per cent	95.1	93.4
Temperature flue gas leaving furnace, deg F	1860	1710
Temperature flue gas entering superheater, deg F	1550	1470
Temperature flue gas leaving boiler, Fig. 2; economizer, Fig. 3	710	617
Flue-gas temperature leaving air heater, deg F	536	426
Flue-gas temperature leaving direct-contact liquor evaporator, deg F	283	286
Total combustion air leaving furnace, per cent	105	105
Gas analysis leaving boiler or economizer:		
CO_2, per cent by volume	15.1	17.2
O_2, per cent by volume	4.8	1.9
CO, per cent by volume	0.16	0.0
Total combustion air leaving boiler or economizer, per cent	128	110
Total combustion air leaving air heater, per cent	147	118
Total combustion air leaving direct-contact liquor evaporator, per cent	147	118

In the higher-temperature zones, temperature measurements were made with high-velocity thermocouples as previously described.

From these data the lower gas temperatures and lower per cent air infiltration obtained on the newer 275 ton/day capacity unit are evident. The air infiltration shown between the furnace and economizer outlet is only 5 per cent of the theoretical air required for combustion.

SOOT BLOWERS

With the easier removal of chemical deposits from the heating surfaces of the newer-type unit and with the numerous cavities

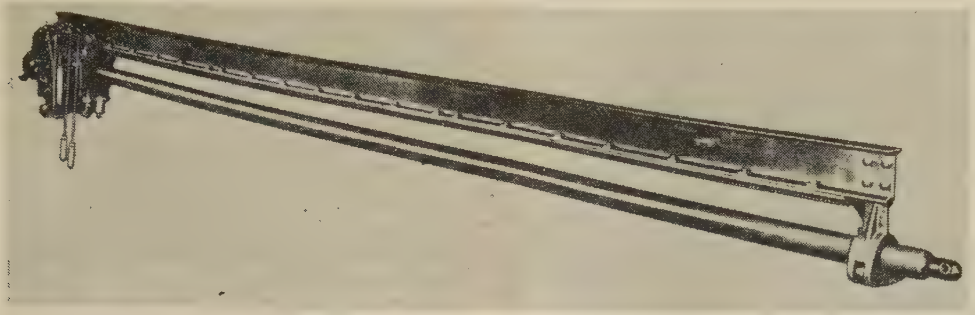

Fig. 6 Retractable-Type Soot Blower

provided in the setting, mechanical soot blowers can be applied successfully to clean the entire unit, eliminating the need for regular crews of men to do hand-lancing.

It has been found that the usual types of fixed-position rotating soot-blower elements, which remain in the setting when not in use, do not have a satisfactory life when installed in the high-temperature zone of the recovery unit. As a result of this, and because of the superior cleaning results obtained, retractable-type blowers have been employed. These blowers are withdrawn from the setting except during the blowing cycle when they are cooled by the blowing medium. The type of retractable blower used is shown in Fig. 6. In place of an element with a multiplicity of small nozzles, an element with two large nozzles at the end is used. During blowing, the element moves inward across the setting and then back, rotating continuously during its travel. Either high-pressure steam or air is used as the blowing medium.

To withstand the high impact provided by the steam or air jets from the two large soot-blower nozzles, and to avoid damage to refractory, it has been found desirable to use metallic gas baffles in place of refractory. In the high-temperature zones, the baffles are made up of flat studs welded to, and cooled by, the boiler tubes.

Typical locations for the retractable blowers in the boiler and superheater are indicated by heavy black circles in Fig. 3. Familiar types of fixed-position rotating soot-blower elements, usually of the air-puff type, are installed as necessary in other locations in the boiler and economizer.

The application of retractable-type soot blowers to recovery units is relatively new; however, it follows established practice in the power-boiler field. For a number of years, retractable-type soot blowers have been used for slag removal in the high-temperature zones of pulverized-coal-fired boilers, and there is a trend toward their use in the lower-temperature zones because they eliminate the need for soot-blower bearings in the gas stream, permit maintenance during normal operation, and have a larger effective cleaning radius than the standard types of fixed-position rotating elements.

The older types of soot blowers for gas-air heaters were not very successful and considerable hand cleaning during operation and outages was often required. "Strait-Line" type blowers are now being used and satisfactory cleaning results are obtained without need for manual cleaning during operation or outages.

An outline of a Strait-Line blower is shown in Fig. 7. The blower is equipped with two nozzles per tube-row blown. It moves continuously inward across the air heater and back while blowing. When not in use, it is withdrawn to the side of the heater. Either steam or air is used as the blowing medium.

In addition to improving the soot-blower equipment for cleaning the gas-air heaters, it has been possible to eliminate the formation of hard chemical deposits in the tubes by using parallel flow of gas and air in place of counterflow. In counterflow designs, hard dense deposits were caused by condensation of water vapor in the flue gases which combined with the chemical dust. The condensation took place at the gas-outlet end of the air heater where the coldest gas, coming in contact with the tubes adjacent to the incoming cold air, was cooled below the gas dew-point temperature. By using parallel flow of gas and air, the tubes adjacent to the cold-air inlet are heated by the hot incoming gas and consequently are maintained above the dew-point temperature of the gas.

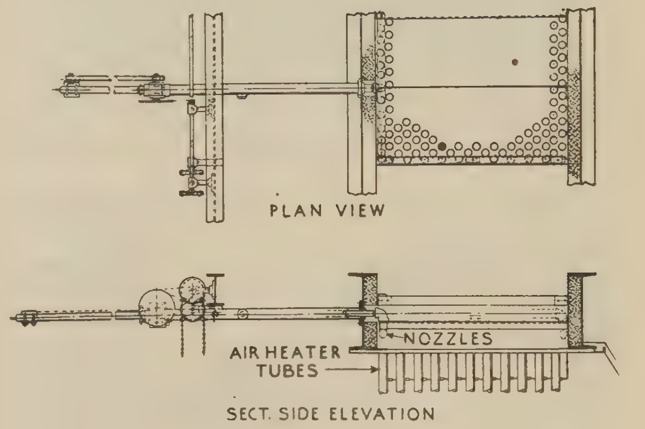

Fig. 7 Strait-Line Soot Blower for Gas-Air Heater

Recovery-System Steam Production

The majority of B&W-Tomlinson units have been equipped with gas-air heaters which give gas temperatures to the direct-contact liquor evaporator on the order of 450-500 F, compared to temperatures of 600-700 F on units without gas-air heaters.

Aside from supplying the hot air necessary for stable furnace operation, the use of a gas-air heater permits a higher net steam generation for the entire recovery system. The net steam generation is considered to be the steam generated by the recovery unit less the steam consumed by the multiple-effect evaporators and liquor heaters. Where a steam-coil air heater is used, the Btu in the steam consumed by the heater is also a deductible item; however, the heat input from the steam to the heater increases the Btu output in the steam from the recovery unit roughly by an equivalent amount. A steam air heater, consequently, has no significant effect on the net Btu output in the steam from the recovery system.

The steam production from a given tonnage-capacity recovery unit, including the direct-contact evaporator, depends upon the following:

1 Heating value of the black-liquor solids.

2 Liquor concentration to the direct-contact evaporator.

3 Gas temperature and unburned combustibles in gases leaving direct-contact evaporator.

4 Gas weight leaving the direct-contact evaporator per pound of black-liquor solids. (This is dependent on the liquor analysis and the excess air in the flue gas.)

It will be noted that with items 1, 3, and 4 constant, the net steam production of the recovery system is affected only by the liquor concentration to the direct-contact evaporator, and that it is independent of the liquor concentration as fired. In considering the thermal performance of a recovery unit, the direct-contact evaporator must be considered as an integral part of the unit. In completely dehydrating liquor which is supplied at a given concentration from the multiple-effect evaporators, prior to combustion, a definite amount of heat is required for the evaporation of the water content of the liquor, the amount being independent of the relative portion of the evaporation done in the direct-contact evaporator and in the furnace.

The net steam production of a recovery system versus the liquor concentration from the multiple-effect evaporators is shown in Fig. 8. The liquor concentration leaving the multiple-effect evaporators has been taken as the concentration to the direct-contact evaporator of the recovery unit. Use of water or weak black liquor for dilution purposes in the direct-contact evaporator would be equivalent to reducing the liquor concentration to it.

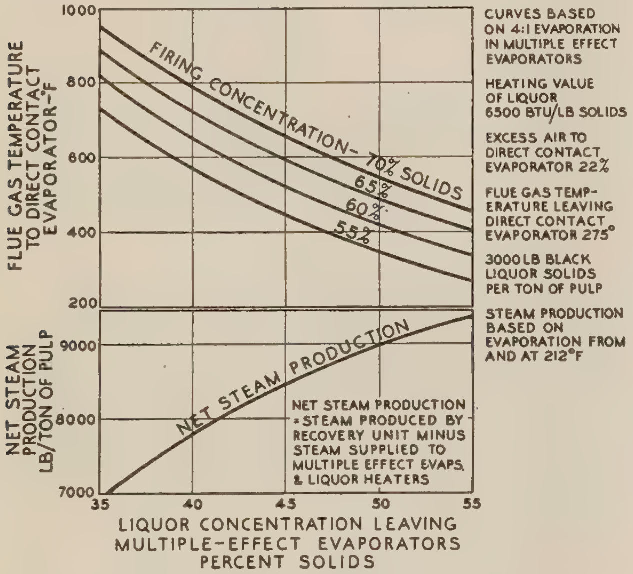

Fig. 8 Recovery-System Steam Production

It will be noted from Fig. 8 that there is an increase in net steam production as the liquor concentration from the multiple-effect evaporators or to the direct-contact evaporator is increased.

Based on a given gas temperature leaving the direct-contact evaporator and a given liquor concentration from the multiple-effect evaporators, the liquor firing concentration is governed by the gas temperature to the direct-contact evaporator, as shown in the upper portion of Fig. 8.

For design purposes, 55 per cent solids is usually considered the minimum firing concentration at which stable combustion can be self-sustained, and 70 per cent solids is usually considered the maximum firing concentration because of handling difficulties due to extremely high liquor viscosities. With these limits on permissible firing concentrations and with given gas temperatures entering and leaving the direct-contact evaporator, the liquor concentration from the multiple-effect evaporators must be held within certain specific limits. With a gas temperature of 450-500 F which might be expected from a unit with a gas-air heater, the liquor concentration from the multiple-effect evaporators can vary from approximately 44 to 54 per cent solids without exceeding permissible firing-concentration limits. With a gas temperature of 600-700 F, which might be expected from a recovery unit without a gas-air heater, the liquor concentration from the multiple-effect evaporators can vary from approximately 37 to 45 per cent solids without exceeding permissible firing-concentration limits. From this it can be seen that the use of a gas-air heater permits employing higher liquor concentrations from the multiple-effect evaporators and consequently permits selection of recovery-system equipment to give a higher net steam production than is possible without it.

In order to realize a substantial increase in net steam production through the use of a gas-air heater, it is necessary to provide sufficient multiple-effect evaporator capacity to concentrate the liquor to 50 per cent solids or higher; however, there is no increase in steam production from high liquor concentration to the direct-contact evaporator where the recovery unit is not designed for it.

As an example, assume a gas temperature of 650 F and a liquor concentration of 50 per cent solids to the direct-contact evaporator. Referring to Fig. 8, this would give a net steam production of 9000 lb per ton of pulp but a liquor firing concentration of approximately 80 per cent solids, which is above the permissible limit. In order to reduce the firing concentration to 70 per cent solids, the liquor in the direct-contact evaporator could be diluted with weak liquor or water, which would be equivalent to reducing the concentration from the multiple-effect evaporators to 45 per cent solids, and would reduce the net steam production from 9000 lb per ton of pulp to about 8400 lb per ton of pulp.

Summary

In the past decade the uses and new applications of pulp and paper products have brought about a tremendous expansion of the industry which has compelled the growth and technical advancement of all component divisions of the manufacturing process. The vital functions of chemical recovery and generation of power and process steam are carried out by the modern recovery unit, which has kept pace with the progress of the industry through the development of new design features and the adaptation of sound engineering developments to provide greater capacity, economy, and reliability in operating service.

Discussion

E. H. Kennedy.[5] Fig. 9 of this discussion gives a side elevation of a waste-heat and chemical-recovery unit which began operation in 1938. It is of the same general design as the 1946 unit which is described in the paper.

As will be noted, this 1938 unit had a tubular gas-air heater. So much trouble was experienced in keeping the gas-air heater clean that it has not been used since on this make of recovery unit. This is not said to disparage the gas-air heater, because most of the trouble was due to the fact that mechanical soot blowers for cleaning the air heater were not provided.

Fig. 10 shows a second unit which began operation in 1940. This is of the same general design as shown in the paper. The principal difference is in the arrangement of the superheater; the nose arch under the superheater is lacking. Accumulations of ash or smelt on the front bank and superheater of this 1940 unit may drop directly into the furnace.

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[5] Chemical Engineer, Paper Mill Equipment Division, Combustion Engineering Company, Inc., New York, N. Y.

Fig. 11 herewith shows a view looking directly up through the front bank and superheater of the 1940 unit; the view which one would get if standing at the bottom of the furnace.

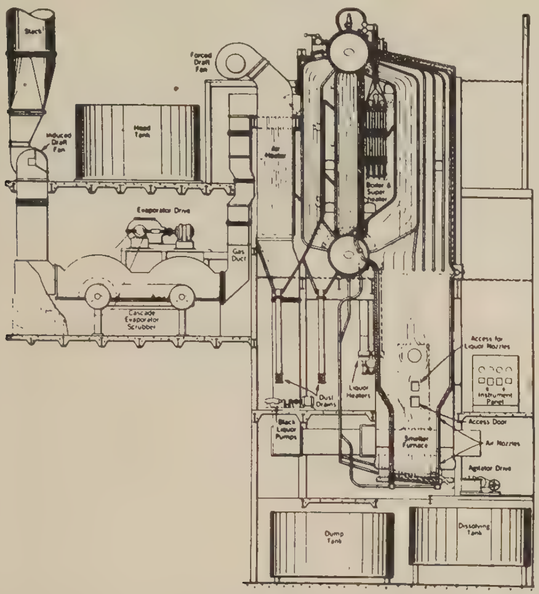

Fig. 9 Waste-Heat and Chemical-Recovery Unit of 1938 Type

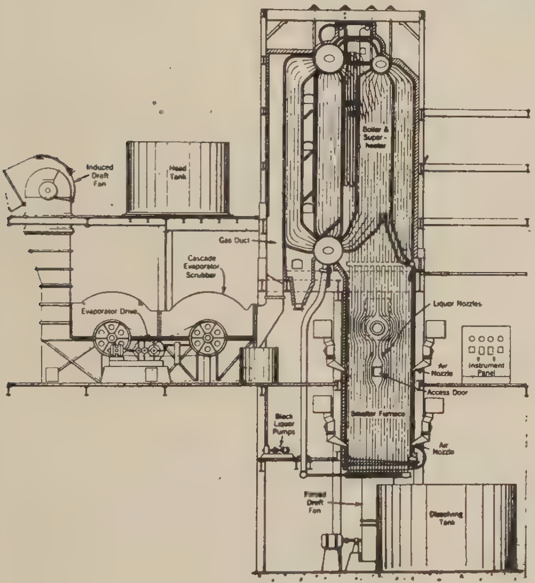

Fig. 10 Unit Put in Operation in 1940

To return to a discussion of the types of air heaters which are used with recovery units, it should not be forgotten that there are several advantages, as follows, which have led to the use of a steam-air heater on many units:

1 It always remains clean and efficient as a heat-transfer unit without the use of mechanical, steam, or air soot blowers.

2 A constant and maximum air temperature is always maintained, even at the start-up.

3 The heat in the steam to a steam-air heater need not be a completely deductible item in the heat balance, because some of the heat (the latent heat) is indirectly returned to the furnace, and some of the heat (heat in the condensate) can be, and in most cases, is returned to the unit by way of the feedwater. Radiation losses, accounting for the balance of the heat in the steam to the air heater, are not available for steam production. Moreover, the steam used in a steam-air heater is usually first passed through a turbine, and energy is extracted to produce electrical power before the steam at 125 psi pressure is used for the steam air heater.

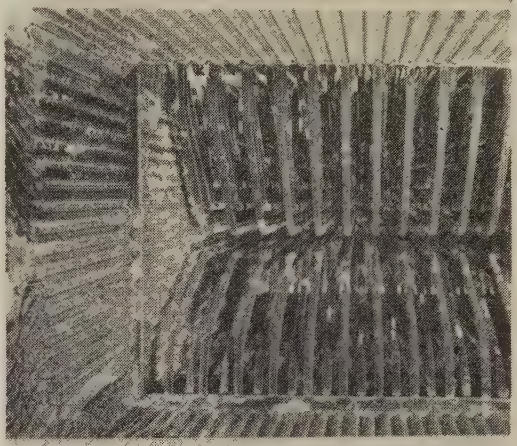

Fig. 11 Superheater and Front Bank of 1940 Unit

It is true that in the past recovery units have been built so that

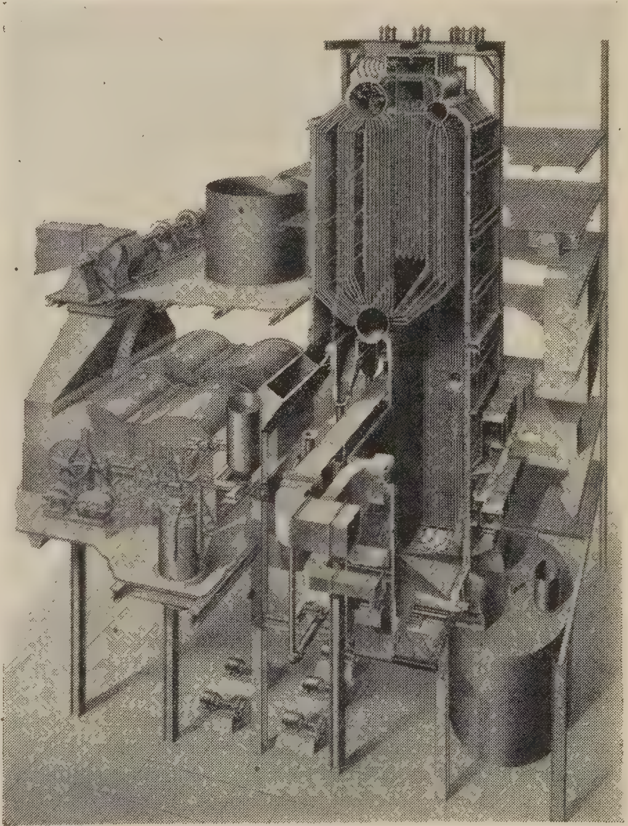

Fig. 12 Modern Waste-Heat and Chemical-Recovery Unit for Kraft Paper Mill

they could not take full advantage of having a high percentage of solids delivered to the cascade evaporator. But it was often fortunate then, because a high percentage of solids could not always be delivered by the multiple-effect evaporators. The cascade evaporator then acted like a flywheel for the recovery system. This does not mean that recovery units having a steam-air heater cannot be designed to take advantage of high solids concentration from the multiple-effect evaporators without subsequent dilution in the cascade evaporator. New units are being designed and have been sold with sufficient surface in the boiler and economizer to reduce gas temperatures entering the evaporator so that dilution will not be necessary when using a high concentration of solids from the multiple-effect evaporators.

Information from the field has constantly been coming in that it is not practically desirable to reduce the exit-gas temperature from a waste-heat and chemical-recovery unit much below 300 F, if an electrical precipitator is to be used after the recovery unit. This is especially true in northern climates where the winters are severe. This does not mean that an exit-gas temperature of 275 F is not possible or, in some cases, practically desirable because the lower exit-gas temperature does mean an increase in thermal efficiency.

It has been shown in Fig. 8 of the paper that for a given percentage of solids in and out of the contact evaporator, a certain gas-temperature drop is required to evaporate the water between these terminal conditions. A difference of opinion is present here, perhaps, because the pounds of gas per million Btu of input were not taken to be the same. Be that as it may, it looks as if it would require about 14 per cent greater gas-temperature drop to evaporate the water between given terminal conditions in the contact evaporator than is shown here. This would mean that the entering-gas temperatures would have to be higher than shown in Fig. 8.

Fig. 12 of this discussion may be of some interest to power-plant engineers who may not be too familiar with a waste-heat and chemical-recovery unit of a Kraft paper mill. Fig. 1 of the paper shows its location in the complete scheme of a Kraft paper mill. Fig. 12 shows in more detail its various parts in perspective.

Author's Closure

The similarity of design suggested by Mr. Kennedy between the 1946 recovery unit, Fig. 3, and the 1938 type, Fig. 9, and the 1940 types, Figs. 10 and 12, is superficial rather than real. All of the designs incorporate a standard arrangement of water-cooled vertical furnace and laterally offset bent-tube boiler. The later developments, such as the superheater nose baffle arrangement and mechanical soot blowers for cleaning the boiler screen, superheater, and air heater, are found only in the 1946 type discussed in the paper.

As already described in the paper, our experience with gas-air heaters not of parallel-flow design would lead us to expect the difficulties ascribed by the discusser to the gas-air heater shown in Fig. 9, particularly when no provision was made for mechanical cleaning.

Past experience with steam-air heaters has not been all that could be desired. Frequent heater-element failures due to internal corrosion have reduced the availability and increased the maintenance so that, in many instances, a steam-air heater would compare unfavorably with a gas-air heater of parallel-flow design. There have been a number of recent improvements in steam-air heater design directed toward reducing element failures and permitting easy element replacement in case of failure. Either type of heater is now believed to be suitable for Kraft recovery-unit service and the question of which to use resolves itself into one of engineering economics. Owing to the necessity of bringing the furnace up to temperature with auxiliary fuel before firing black liquor, preheated air is available at start of black-liquor firing when using a gas-air heater.

The question raised regarding the evaporation in the direct-contact evaporator for a given gas temperature drop shown in Fig. 8 is understandable as there are several other factors besides the temperature drop which affect the evaporation. These include the gas quantity per million Btu mentioned in the discussion, the air infiltration into the evaporator, the radiation loss, and the liquor temperature entering and leaving the evaporator. The relations shown in Fig. 8 were based on using a cyclone evaporator as shown on Fig. 1 which is airtight and has a low radiation loss. The following test data, Table 2, on two different types of evaporators is illustrative of the difference in evaporation.

TABLE 2 DIFFERENCE IN EVAPORATION IN CASCADE AND CYCLONE DIRECT-CONTACT EVAPORATORS

Unit Size	250 ton/day				275 ton/day	
Type Evaporator	Cascade				Cyclone	
Unit rating during test, ton/day	175	172	223	208	197	256
Liquor concentration to evaporator, per cent solids	40.2	41.3	41.3	40.0	47.9	47.3
Liquor concentration leaving evaporator, per cent solids	58.1	61.4	64.3	57.0	56.8	57.6
Gas temp. to evaporator, deg F	656	635	643	611	392	445
Gas temp. leaving evaporator, deg F	245	236	207	241	247	279
Total combustion air to evaporator, per cent	123	128	124	128	114	119
Total combustion air leaving evaporator, per cent	..	..	..	135	114	119
Equivalent gas temperature, deg F, entering evaporator based on correcting exit gas temperature to 275 deg F	686	674	711	645	420	441
From Fig. 8, the entering gas temperature required for the evaporation shown, deg F	615	645	670	600	415	435

From these data it will be noted that, for the cascade evaporator, the gas temperature drop is 12 per cent greater than that shown on the curve; however, the gas temperature drop for the cyclone evaporator agrees with the curve. The higher gas quantity per million Btu as evidenced by the higher excess air entering the cascade evaporator would be expected to reduce the gas temperature drop required, however, this is more than offset by radiation and air infiltration. The radiation and air infiltration represent thermal losses which are reflected in lower steam generation.

Although not submitted for publication other discussers raised questions on the following:

1 Discuss known factors limiting capacity, steam temperature, and design pressure of recovery units:

One factor limiting capacity is the maximum width of boiler which can be cleaned by hand-lancing in case of emergency. At present, units with capacities up to approximately 500 ton per day can be built without exceeding this or other known limitation.

To date we have not built units for steam temperatures above 750 F, however, there has been considerable demand recently for higher steam temperatures, and development work is in progress to establish alloys suitable to meet these requirements.

The developments in recovery unit design have closely followed power-boiler development where ability to maintain adequate boiler circulation and high steam purity over a very wide range of design pressure has been obtained. Many power boilers are in successful operation at pressures of 1500 psi and it would be practical to design recovery boilers for similar pressures.

2 Discuss methods of maintaining proper air distribution between primary and secondary air nozzles:

A controller to automatically maintain the proper air distribution between primary- and secondary-air nozzles has been in satisfactory service on a 275 ton/day unit for more than a year. The controller is actuated by the relative air flows rather than air pressures so that variations in nozzle pressures due to slagging over of the nozzles or readjustment of the nozzle openings will not affect the air distribution. Controllers to automatically maintain a constant total air flow are also available but have not yet been used.

3 With a gas-air heater, the temperature of air leaving the heater varies directly with the outside-air temperature. Is maintenance of a constant air temperature to the furnace justified in order to reduce excess deposits on the boiler tubes?

A constant air temperature will eliminate one operating variable. There are a number of others such as rate of salt-cake make-up and rate of hopper dust return which are believed to have a more pronounced effect on furnace performance. Efforts to maintain these constant might be expected to contribute more toward good furnace performance than the constant air temperature.

4 Discuss elimination of metal casings on recovery units:

In the past casings have been provided to obtain a tight boiler setting and to prevent damage to insulation during hand-lancing. At present tight settings can be obtained without the casing. The application of mechanical cleaning equipment to replace hand-lancing should make elimination of the casing practical.

Utilizing Bagasse as Fuel

By F. X. GILG,[1] NEW YORK, N. Y.

Modern boilers and bagasse-burning furnaces for steam generation in sugar mills are described in this paper. Performance of an integral-furnace boiler with Ward furnaces is given and includes fly-ash carry-over tests.

In the production of sugar from sugar cane, large quantities of steam are required to cook and evaporate the moisture from the juice which eventually becomes crystallized sugar. Large quantities of steam are also required to drive the heavy rolls that squeeze the juice from the sugar cane. Through one of those fortuitous circumstances of Nature, the fibrous residue from sugar cane is combustible and provides more than enough fuel to generate the steam required to produce raw sugar. This fibrous residue is called "bagasse."

The purpose of this paper is to describe some of the furnaces and boiler equipment which are specially designed for sugar-mill service.

Bagasse looks and feels like damp "excelsior," the shredded-wood packing material used to protect fragile articles in shipment. In some mills which do not shred the cane before feeding it to the squeezing rolls, the bagasse contains coarse pieces that are like crushed corn stalks. Like most other solid fuels, the finer the bagasse is divided, the easier it is to burn. The moisture content varies from 45 to 55 per cent, depending on the type and efficiency of the squeezing equipment. Despite its high moisture content, bagasse burns very easily on the surface of an incandescent pile in specially designed furnaces containing sufficient hot brickwork to drive off the moisture and having the correct facilities for introducing combustion air in proper quantities and direction.

During the early days of sugar making, bagasse was dumped out in the fields, to be sun-dried and then brought back into the boiler plant to be shoveled into furnaces as fuel under kettles or boilers. To reduce the labor of handling such a bulky fuel as bagasse, some resourceful pioneer tried burning the "green bagasse" directly as it came from the mill and discovered that green bagasse would burn satisfactorily in a "Dutch-oven" type of furnace with natural-draft grates. This development opened the field to numerous inventors who produced many different shapes of furnaces and grates. However, the most successful ones depended upon burning the bagasse on the surface of a pile aided by reflected heat from hot brickwork, air for combustion coming up through the grates. Most of these bagasse-burning furnaces have been described by Prof. E. W. Kerr.[2]

Early Designs of Furnaces

There are many of these early furnaces with grates still in use today. Some operate on natural-draft air through the grates, but for higher capacity forced draft is necessary. Grates have always been a source of trouble in that they become clogged, thus reducing the area for air passage and adversely affecting the capacity. Grate maintenance is high because of the lack of cooling air passing through them when clogged. Grate maintenance is aggravated by the heat from partly burned siftings that continue to burn underneath the grates. Also, the forced-draft pressure under the grates results in excessive amounts of bagasse being blown off the fuel pile and carried off with the products of combustion.

The hearth or grateless type of furnace was developed to overcome the troubles with the grate-type furnaces. They still retained the essential feature of burning the bagasse on the surface of a pile. The air for combustion, however, was admitted horizontally through tuyères in the vertical walls surrounding the hearths.

Some of these early Dutch-oven designs became very large. In one particular design a single large Dutch oven was installed between two boilers, each boiler being traversed by one half of the products of combustion. The roofs over the Dutch ovens were made of sprung arches which required maintenance and replacement. Also, the large wall areas of these furnaces and the increasing cost of brickwork, the high radiation loss from the large areas of brickwork, the loss of steam pressure when these large furnaces were cleaned, led inventors to consider smaller furnaces. Eventually, the Cook or horseshoe type of furnace was developed, arranged in multiple units under the boiler to permit cleaning without too much drop in steam pressure. The horseshoe shape was chosen to facilitate the cleaning of the hearth through one door located at the front of each hearth. The horseshoe furnace remains the basis of most of the better designs of bagasse furnace.

Boiler Tests With Bagasse Fuel

Many boiler tests have been run in several plants over a period of years with steam output generally at rated boiler horsepower and sometimes less. Efficiencies ranged from 50 to 60 per cent with "radiation and unaccounted for" losses as high as 20 per cent. The loss of efficiency, due to evaporating the moisture in the fuel and moisture formed by the burning of hydrogen in the fuel, was of the order of 20 to 25 per cent. The radiation losses were high because the total heat radiated from the large areas of exposed brickwork is practically constant at all ratings, and its effect on a percentage basis was high because of the low rating at which the boilers operated on natural-draft stacks. The radiation losses were overemphasized to some extent because they were not actually measured, being grouped with "unaccounted" losses, the catch-all item that is left after some easily measured losses and efficiency are subtracted from 100 per cent. The usual method used to determine bagasse weight on a boiler test was to use the sugarhouse figures of weighed cane and metered juice extraction, leaving bagasse as the residue. A check on this weight could be obtained from the weighed cane and its fiber content from a chemical analysis. The unaccounted loss would include such items as unburned combustible in the refuse, fly-ash carry-over and incomplete combustion due to CO in the products of combustion.

Low boiler efficiency, resulting from the burning of wet bagasse as fuel, did not usually present a problem because most sugar mills had more bagasse than they needed. Only in a poorly balanced sugar mill or in a sugar mill that refined its own sugar, produced alcohol, or otherwise used extra fuel for power or pumping purposes, was there a need for more efficient burning of bagasse. An excess of bagasse presents a real problem of disposal which is most easily met by inefficient burning.

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[1] Application Engineer, Babcock & Wilcox Company. Mem. ASME.

[2] "Bagasse Furnaces," by E. W. Kerr, Trans. ASME, vol. 61, 1939, pp. 685–691.

Contributed by the Fuels Division and presented at the Spring Meeting, New Orleans, La., March 1–4, 1948, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 48—S-3.

Included in Professor Kerr's paper[2] was a description of the newly developed Ward single-pass furnace. Since that time, hundreds of Ward single-pass furnaces have been installed in Mexico, Central and South America, Cuba, Puerto Rico, the Dominican Republic, and Haiti. The principal features of this furnace are the elimination of costly arches over Dutch ovens, a reduced amount of costly brickwork, the absence of grates and their maintenance. In addition to these advantages from a construction standpoint, there is a very important advantage from an operating standpoint in that these furnaces can be operated continuously because the refuse can be removed while the boiler is in service. There is no slag formation in the secondary combustion chamber above the hearth, and therefore it is not necessary to shut the unit down periodically to clean or remove this slag as is common practice on almost any other type of high-capacity unit.

Details of the Ward Furnace

Fig. 1 shows the general shape of the Ward furnace as it is applied to a modern Stirling boiler with air heater, forced- and induced-draft fans. The position of the furnace in relation to the boiler tubes makes it possible to shield the furnace with a short arch, thus simplifying the structure.

There is some carry-over of particles of partly burned bagasse at high rates of combustion. These particles continue to burn as embers on their way through the boiler gas passages. Collecting hoppers can be provided at turns in the boiler gas passes from which the carry-over can be picked up with a steam- or air-aspirating system as shown, and returned to the furnace for burning. This arrangement improves the efficiency not only by virtue of fuel recovery but also by providing turbulence for better mixing of combustible gases and air for combustion in the furnace proper. In plants where economy of fuel is not a factor, the carry-over is permitted to settle out and is removed manually during each shift.

To improve the heat absorption and reduce consumption of scarce fuels such as coal, oil, or gas, the tube spacing of modern boilers has been reduced, resulting in increased draft loss. On costly fuels, such as coal, oil, or gas, the cost of an induced-draft fan can be justified because it permits economical high-capacity

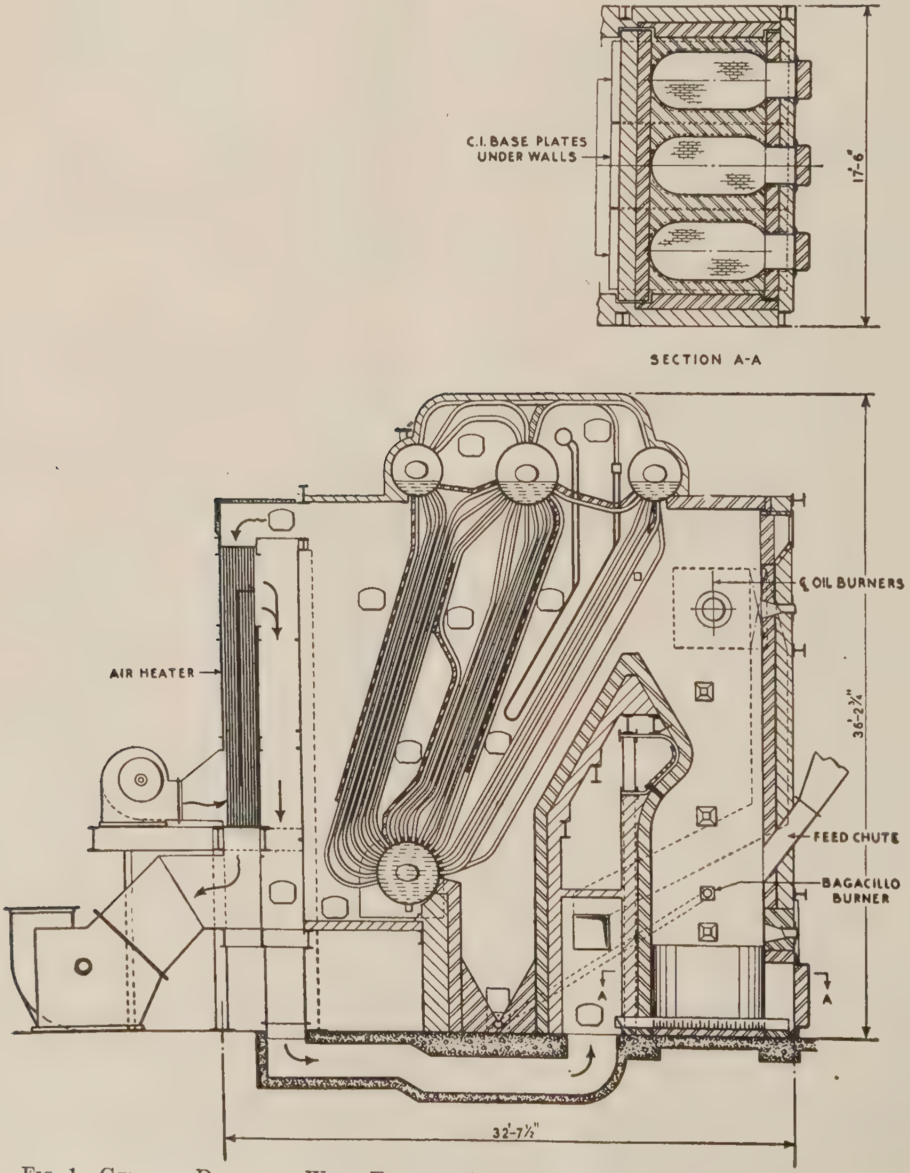

Fig. 1 General Design of Ward Furnace Applied to Modern Stirling Boiler

operation. Most sugar mills operate only a few months a year. Using a by-product fuel, fans, and air heaters cannot always be justified. Therefore there was a real need for a bagasse-burning boiler of a design which would permit operation on natural-draft stacks. Fig. 2 shows a design of boiler with a minimum number of baffles arranged so that the major part of the draft loss is created by products of combustion passing over the heating surface with practically no draft loss at the gas turns. Therefore the draft loss is about one half of what it would be with a standard three-pass baffling shown in Fig. 1, and permits operation of 200 per cent rating with stacks about 150 ft high.

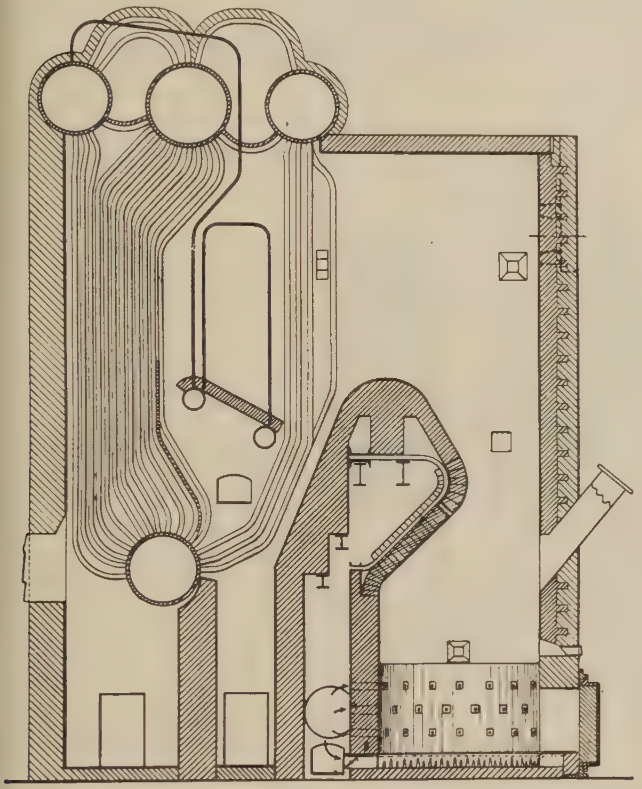

Fig. 2 Boiler Design With Minimum Baffling

The furnace above the bagasse furnace is large enough to permit the installation of oil burners for stand-by service during temporary mill shutdowns. The burning of oil at high capacity in bagasse furnaces causes severe slagging troubles which can be minimized in this design by the installation of water-cooled furnace walls.

Since the development of this boiler in 1944 about 40 sugar mills have installed this type of boiler and Ward furnace combination. Typical performance of this unit is as follows:

Steam flow (135 per cent rating), lb per hr	40,000
Steam pressure, psi	200
Steam temperature, deg F	440
Temperature of gas leaving boiler, deg F	645
Draft loss, boiler and superheater, in. H_2O	0.6

Integral-Furnace Type of Boiler

In those sugar mills which refine their own sugar or which generate power in excess of that required in the mill, requiring supplementary fuel such as oil or gas, an integral-furnace type of boiler with completely water-cooled walls and floor can be arranged for firing bagasse, oil, and gas.

Fig. 3 shows such a unit installed in a sugar mill and starch plant in Florida. It was designed to operate at 650 psi and 725 F total temperature when generating 100,000 lb of steam per hr on oil or gas and 70,000 lb of steam per hr on bagasse. Peak loads of 120,000 lb per hr have been carried on either fuel. The high-pressure high-temperature steam is passed through a turbine which discharges steam into the 180-lb header serving the sugar mill.

Bagasse is dropped on the hearth of the three Ward furnaces through a chute in the front wall, forming a conical pile about 5 ft high. Hot air for combustion is forced horizontally into the base of the pile from air slots in a base plate completely surrounding the hearths, which are 5 ft wide and 7 ft long and have rounded corners. Air for combustion is also forced into the pile higher up through three rows of tuyères. The feed of bagasse is continuous, falling on a pile in each hearth, igniting from the reflected heat of the hot brickwork. The bagasse burns vigorously on the surface of the piles. At steam flows above 60,000 lb per hr, some of the partly burned fuel is blown off the pile and continues to burn in suspension on its way to the main furnace and the boiler gas passes, a distance of about 36 ft. Some of the particles drop out of suspension onto the water-cooled floor of the main furnace, which is fitted with three rows of pinhole grates supplied with air for combustion under damper control. Once each day the ashes, which are dry and loose, are blown into the ash trench at the rear of the furnace with an air lance. There is no slagging trouble whatever. The unit operates continuously from the beginning to the end of the processing of the crop. Once each day, the feed to each hearth is shut off for a few minutes to permit burning down the pile and removing ashes through the cleanout door in the front of each hearth. This cleaning operation does not affect the steam pressure which is maintained by increased burning in the other two cells.

The unit is equipped with automatic combustion control and a complete set of indicating and recording meters and instruments to show the operators exactly what the unit is doing, and as a guide in its operation. Efficient operation is necessary at all times because this unit supplies the needs of the sugar plant as well as the starch plant. The feed of bagasse is controlled from a main gate in the overhead bagasse conveyer by an automatic control device operating from steam pressure. One oil burner burns oil continuously at its minimum setting to maintain its ignition. When the supply of bagasse is insufficient to maintain steam pressure, as evidenced by the wide-open position of the feeder gate, the automatic combustion control increases the flow of oil to the oil burner. Each oil burner can burn enough oil to generate 60,000 lb of steam per hr, sufficient to take the load swings on one burner. However, if the supply of bagasse is completely interrupted, the operator inserts a second oil burner. When the bagasse feed is restored, the steam pressure rises and the oil pressure is automatically reduced to its minimum setting and the load is again carried on bagasse. Air for combustion of bagasse and oil is controlled automatically and in proper ratio by metering orifice plates which meter the air in proportion to the fuel flow. The induced-draft fan is regulated automatically to maintain the furnace draft at all steam outputs. During the off season when bagasse is not available, full load is automatically maintained on oil fuel.

The oil burners are equipped with gas rings to burn methane gas, a by-product of the starch plant.

Controls of the entire unit are equipped with safety interlocks, including an electric eye in the oil burners, so that the motor drives can be started in proper sequence to insure proper purging of the setting before lighting-off oil or gas. In the event of fuel or fan failure, the motor driving the fans and fuel pumps will be tripped out in proper sequence to avoid hazardous conditions. In the event that fuel-oil flow is interrupted or ignition is other-

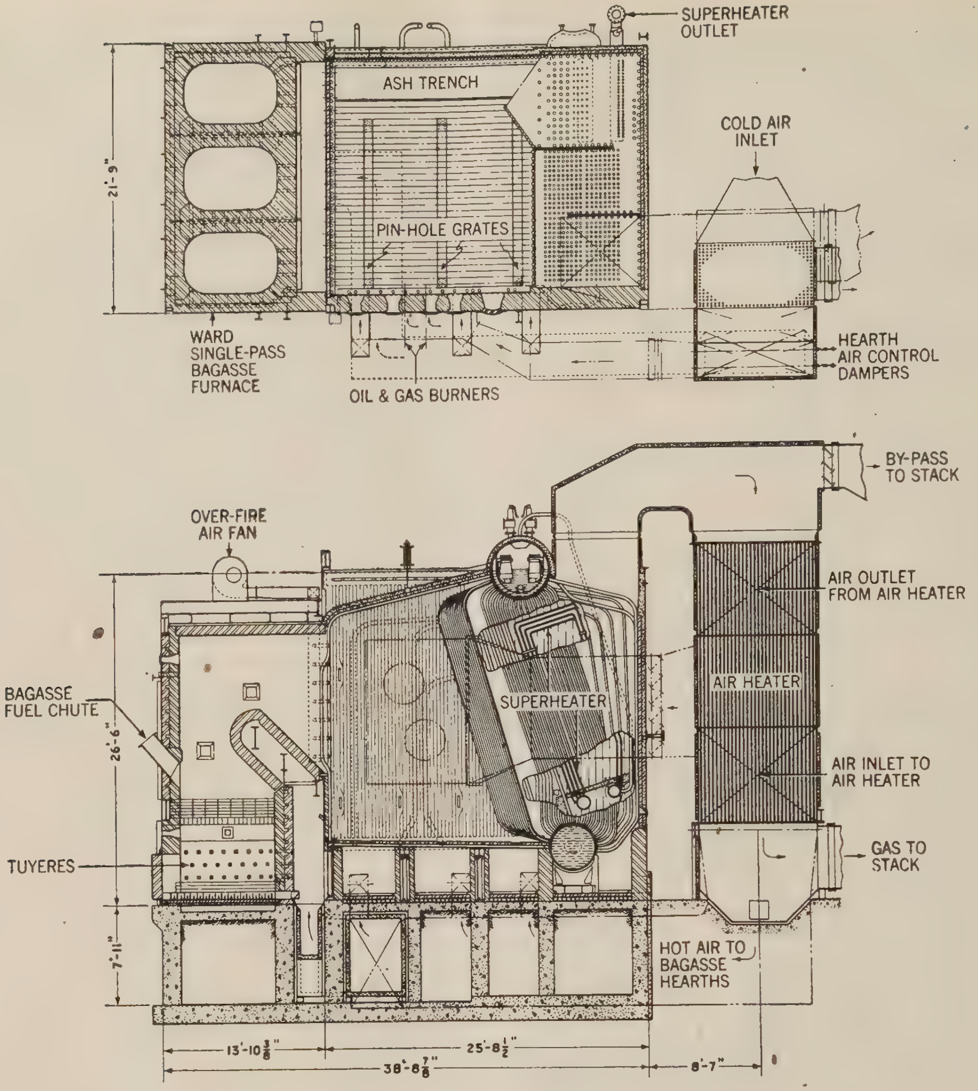

FIG. 3 INTEGRAL-FURNACE UNIT FOR SUGAR MILL

wise interrupted, the electric eye shuts off the fuel supply valves and the forced-draft fan.

This installation has been in service for 2 years at high capacities, firing bagasse during the sugar-grinding season and oil during the off season. The performance with oil fuel is in line with the expected performance from hundreds of similar units burning oil in integral-furnace boilers. On test at a steam flow of about 100,000 lb of steam per hr, the measured efficiency was 83.3 per cent.

The performance on bagasse as fuel was excellent and even exceeded the expectations on capacity. It seems that the combustion actually improved with higher burning rates because of higher furnace temperatures and greater turbulence. Actually, steam flows as high as 120,000 lb of steam per hr have been carried on bagasse with excellent results, despite the high moisture content of 52.25 per cent. The hot air for combustion, of approximately 500 F, of course had a great deal to do with the excellent combustion results.

Even at the high steaming rates, the carry-over of partly burned bagasse was much less than experienced in this same plant on other boilers and furnaces, operating at much lower steaming rates. Inasmuch as the carry-over of partly burned bagasse in stack discharge may be a nuisance to a community and a loss in efficiency as well, arrangements were made to measure the fly-ash loss from this boiler.

As shown in Fig. 4, this boiler has its own stack, which therefore provides a convenient place for measuring the concentration of fly ash in the stack discharge in a section above the roof. Consistent results can be obtained at this point because the mixing action in the induced-draft fan precludes stratification. A nine-point sampler was used to obtain representative samples.

The complete test data taken during four tests are given in Table 1.

TESTS SHOW EXCELLENT PERFORMANCE OF UNIT

From these test data it will be seen that the amount of refuse in the products of combustion leaving the unit at a steaming rate of 70,000 lb of steam per hr is less than 1 per cent of the as-fired fuel, representing a loss of efficiency of 0.7 per cent. At higher steaming rates of course the fly-ash carry-over increases but, even at 86,500 lb of steam per hr, the loss in efficiency is only 1.8 per cent.

The general performance of the boiler is in line with what was expected except that, because of the high moisture content of 52.25 per cent, it was necessary to operate with more air for combustion than is ordinarily used. The total air for combustion, as

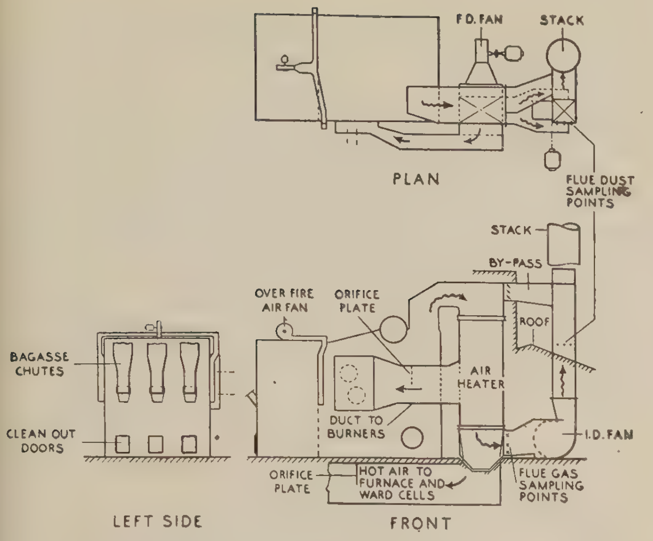

Fig. 4 Bagasse-Fired Boiler With Stack in Which Fly-Ash Carry-Over Was Measured

shown in Table 1, was measured at the air-heater outlet. Therefore this figure includes the air infiltration into the furnace, boiler setting, and flue between air heater and boiler outlet. The principal sources of air leakage into the setting were the large feed chutes which were open to the room, permitting large quantities of air to enter the furnace with the bagasse.

From the heat-balance figures it will be noted that the major losses occur because of evaporating the high moisture content in the fuel and the burning of hydrogen. The heat loss in the dry products of combustion could be reduced with lower excess air but there is nothing that can be done with the high moisture loss except by predrying the fuel. Even with the minor unburned combustible loss as shown by the heat balance, the efficiency is quite low compared to efficiency on other fuels. However, from the standpoint of burning fuel containing 52.25 per cent moisture, it is almost as good as it is possible to obtain except for possible gains which might be experienced by operation with less excess air. For each 15 per cent reduction in total air, an increase of about 1 per cent in efficiency can be expected.

Predrying of bagasse has been discussed for many years. For instance, Professor Kerr ran some tests on drying bagasse in 1911, which indicated a general improvement in economy, using the products of combustion as the drying medium. However, driers have not been used in sugar mills because their cost could not be justified due to the low load factor in such plants. In other words, there can be no justification for spending a lot of money for equipment when by-product fuel is used, and when the equipment is in service only a relatively short time during the year.

Drying Bagasse to Improve Efficiency as Fuel

With the fuel situation becoming more critical all over the world, it is quite possible that some sugar mills, particularly those which refine their sugar, will find it advantageous to exhaust fully the possibilities of utilizing more of the Btu value of their bagasse by removing some of its moisture before it enters the furnace. Heretofore, all investigations into the feasibility of drying bagasse with products of combustion have resulted in the general conclusion that the most economical way to dry the bagasse is to do so in the furnace. However, this conclusion may not be true with conditions as they are today.

TABLE 1 TEST RESULTS ON INTEGRAL-FURNACE BOILER

Analysis of bagasse, per cent:

Moisture	52.25	Carbon	23.0
Volatile matter	40.20	Hydrogen	2.8
Fixed carbon	5.90	Sulphur	trace
Ash	1.65	Oxygen plus nitrogen	20.3
Total	100.00	Ash	1.65
		Moisture	52.25
		Total	100.00

Steam flow, lb per hr	56500	70400	75600	86500
Bagasse, lb per hr	27500	33000	35000	41300
Bagasse, lb per hr per sq ft	291	349	370	437
Steam pressure in headers, psi	623	639	629	619
Steam temperature, deg F	623	637	639	639
Total air at air-heater outlet, per cent	201	169	159	153
CO_2 in flue gas at air-heater outlet, per cent	10.5	12.0	12.7	13.2
Temperature of gas at boiler outlet, deg F	680	702	700	732
Temperature of gas at air heater outlet, deg F	505	520	516	530
Temperature of air to air heater, deg F	98	100	101	100
Temperature of air from air heater, deg F	482	491	483	516
Draft in W. C. furnace, in. H_2O	0.1	0.03	0.09	0.05
Draft at boiler outlet, in. H_2O	1.9	2.1	2.3	3.1
Draft at air-heater outlet, in. H_2O	5.2	5.8	6.3	8.2
Pressure in bagasse windbox, in. H_2O	+1.7	+2.5	+3.1	+3.7
Heating value; bagasse as fired,	3900 Btu per lb			
Refuse in stack discharge, lb per hr	155	272	392	733
Refuse in stack discharge, per cent of fuel fired	0.564	0.824	1.12	1.73
Combustible content, per cent	40.5	24	31.9	26.7
Loss in efficiency, per cent	0.9	0.7	1.0	1.8
Heat balance:				
Heat loss in dry products of combustion, per cent	13.3	11.3	10.5	11.0
Heat loss due to H_2O in fuel, per cent	23.6	23.7	23.6	23.9
Heat loss due to H_2O in air, per cent	0.3	0.3	0.3	0.3
Heat loss due to unburned combustible matter, per cent	0.9	0.7	1.0	1.8
Heat loss due to CO in flue gases, per cent	0.0	0.0	0.0	0.0
Heat loss due to radiation from unit, per cent	1.3	1.0	0.9	0.8
Efficiency of unit, per cent	60.6	63.0	63.7	62.2
Total	100.0	100.0	100.0	100.0

With partially dried bagasse, an economical way to burn bagasse would be in pulverized form in an integral-furnace type of boiler using circular burners which could be equipped with supplementary oil burners. Such a simplified combination oil-and-bagasse-burning unit would eliminate completely the necessity for any extension furnace. Efficient combustion would take place in the water-cooled furnace, in turbulent burners using a minimum of excess air. The efficiency of such a unit could be about 80 per cent in line with the best practice with other fuels such as coal or oil.

Discussion

Otto de Lorenzi.[3] This paper is valuable in that it presents operating and test data, together with an outline of some recent progress in furnace designs for burning wet fibrous fuels. In these newer furnaces, a considerable proportion of formerly used refractory construction is eliminated. Of particular interest are the newer, so-called, Ward furnaces shown as parts of the units in Figs. 1, 2, and 3 of the paper.

In the paper by E. W. Kerr,[2] referred to by the author, the original Ward furnace is illustrated and described. Fig. 5 of this discussion is taken from this paper. The design is therein described in part as follows: "The special features of this furnace are (1) the bottle shape narrowing down to 18 in. at the neck, (2) cast-iron horseshoes through which the air is admitted, etc., etc." All patent claims for this furnace, as we recall, say that the primary combustion chamber below the neck is larger in volume than the secondary chamber above it. Mr. Kerr also indicates that up to 1939, this was the recognized Ward-type fur-

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[3] Director of Education, Combustion Engineering Company, Inc., New York, N. Y. Fellow ASME.

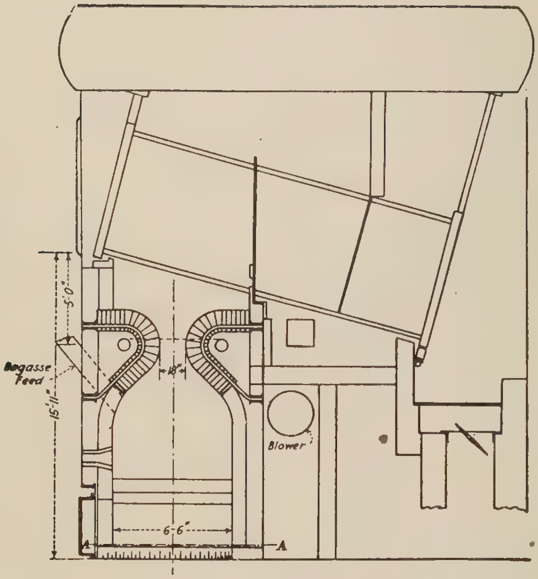

Fig. 5

nace in use. The present author does not indicate when the design was modified to conform with present-day construction.

During the early part of 1937, we visited a number of Cuban and Porto Rican sugar mills, and at that time suggested to several millowners the use of a furnace design which is shown in Fig. 6 of this discussion.[4] The furnace employs the refractory horseshoe construction with rear arch, and a secondary combustion chamber which is larger than the primary. The general design features are almost identical with those of the newer, so-called, Ward furnace shown in the present paper. We are therefore quite pleased to find that this design, as used by others, has proved to be so satisfactory to them.

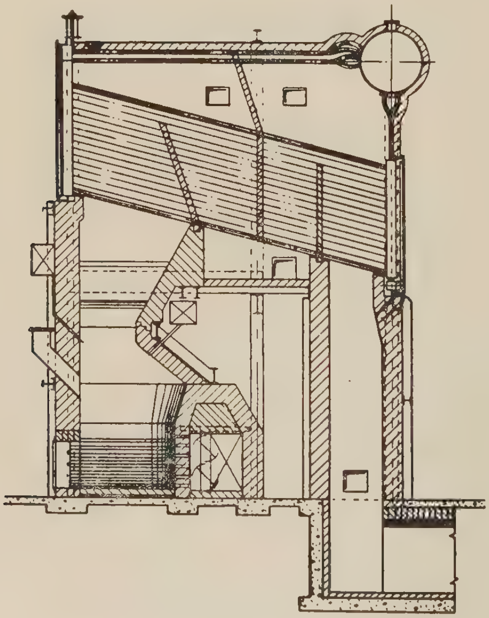

Fig. 6

The most recent improvements for bagasse burning now include a partially water-cooled furnace construction in which Dutch-oven extensions, partition walls, arches, horseshoe-shaped cells, and refractory hearths are eliminated. Spreader-stoker units, in connection with a specially developed feeder, are used to distribute the bagasse onto either dumping or continuous-discharge-type grates, thereby employing the combined principles of flash-drying, suspension-burning, and in-position burning. The fuel bed is thin, uniform, and actively burning over the entire grate. The grate surface extends continuously across the length and width of the furnace, there being no partition walls, arches, or other space-consuming refractories.

A complete bagasse combustion system of this type has been described by H. G. Meissner.[5] Fig. 7 of this discussion is taken from this source. Carefully conducted tests and extended operating experiences have shown increased efficiency, reduced carbon and radiation loss, as well as the ability to maintain easily a close control of fuel-air ratio either manually or automatically. Boiler and furnace availability are improved to the extent that these units may be kept on the line continuously throughout the grinding season.

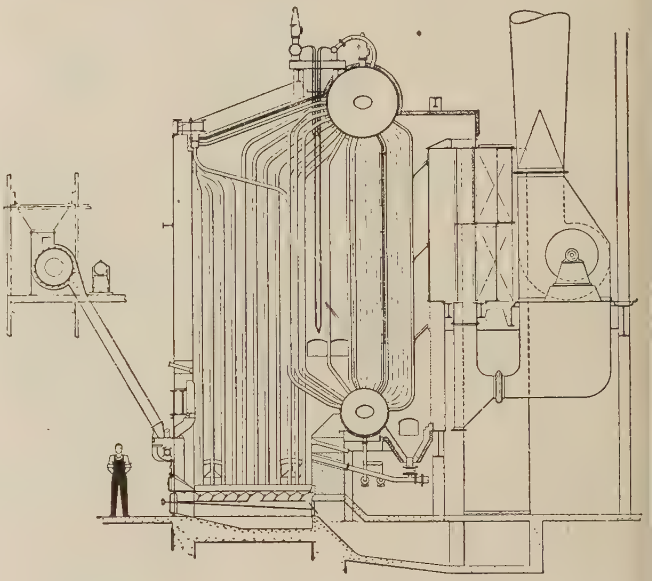

Fig. 7 Spreader-Stoker-Firing System Applied to Two-Drum Boiler

E. L. Dennis.[6] The author briefly reviews the development of furnaces for burning of sugar-cane bagasse, referring specifically to the paper presented by E. W. Kerr.[2] In his paper Professor Kerr gave the bibliography of development of bagasse furnaces and we believe it is appropriate to mention that the present horseshoe-type furnace with tuyère walls probably preceded the many types of grates on which bagasse was burned, and, as the author stated, performed with varying degrees of satisfaction.

For many years the majority of bagasse furnaces were installed with some particular type of grate bars, either flat or inclined. There still remain in many countries various types of furnaces using grate bars instead of the horseshoe-type furnace.

With more study given to the distribution of air to bagasse being burned on hearths in a conical pile, very rapid rates of combustion have been secured without undue carry-over either of unburned carbon or fly ash. As a matter of fact, on horseshoe-type furnaces, a burning rate up to 650 psf of hearth area has been obtained.

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[4] This illustration is taken from "Fuel Burning and Steam Generation," by Otto de Lorenzi, Montreal, Can., 1940, Fig. 204.

[5] "Burning Bagasse at Cuban Sugar Centrals," by H. G. Meissner, *Combustion*, vol. 19, Jan., 1948, pp. 26–31.

[6] President, E. L. Dennis Engineering Company, Baton Rouge, La. Mem. ASME.

In this paper the author states, "Like most other solid fuels, the finer the bagasse is divided, the easier it is to burn." We would agree with this statement of the author provided it was modified by stating that the fuel would contain less than 50 per cent moisture and would not be contaminated with excessive mud and trash which are encountered, particularly in cane fields where the cane is harvested mechanically.

It has been observed that too finely divided bagasse, when burned in any type of furnace, will carry over more unburned carbon and fly ash than when the bagasse is not divided as finely. There is a certain degree of fineness required but, in our observations, we have found that bagasse which is not shredded before milling will allow for deeper penetration of the air blasts from the tuyères and will burn more rapidly and with less carry-over than is the case where wet bagasse is divided into fine particles. In Louisiana, where most of the cane is harvested mechanically, a great amount of field dirt is brought into the factory, particularly in the rainy seasons such as was experienced in November of the past grinding season. We have observed that where an excessive amount of dirt is brought to the factory, most of this will go to the furnaces with the bagasse. At times the conical pile of bagasse will glaze over by fusion of the sand in the bagasse pile. This results in a "killing" effect on combustion of the bagasse. On the other hand, it is almost impossible to burn bagasse, which is contaminated with field mud, on grates. Therefore such furnaces as the Ward furnace, or other modifications of the horseshoe furnace, in all cases give far more satisfactory performance than can possibly be accomplished on any type of grate furnace we have seen in service.

There have been developments in various designs of horseshoe-type furnaces other than the Ward furnace which give remarkable combustion results, and we believe there will continue to be a development in this direction.

As the author well states, in the past a great deal of thought had been given to drying of bagasse partially before combustion by utilizing the waste heat of the stack gases. It would seem that some feasible method will be worked out in this direction in factories where bagasse does not provide all of the fuel necessary for operation.

The author states that with partially dried bagasse, an economical way to burn it would be in pulverized form in an integral-furnace type of boiler, literally by burning it in suspension.

In order to pulverize bagasse it is essential that the percentage of moisture be reduced below 20 per cent unless excessive horsepower is employed. The peculiarities of the fiber in bagasse are such that it will pulverize easily with extremely high moisture contents, and that at intermediate moisture contents of 22 to 50 per cent the power required to pulverize would be prohibitive. On the other hand, bagasse dried to 10 to 12 per cent moisture readily pulverizes without extremely high horsepower requirements. We believe that the value of bagasse as fuel is such that it will not be feasible for many years to anticipate pulverizing and burning in suspension.

One major company at the present time is experimenting in a commercial way firing bagasse on a spreader-type stoker and is claiming favorable results. Within a few years we expect to hear more of the results of these commercial tests. Another company has developed a multicell furnace which is installed directly under the boiler proper in two banks so that the bagasse is burned in cupolas, also a modification of the horseshoe furnace, and fed in a similar manner to the Ward furnace. In this particular type of furnace the floating particles of burning bagasse have to rise to a height of 20 to 25 ft before entering the convection section of the boilers, and in performance the amount of unburned carbon is reduced to a negligible amount. The fine fly ash that is carried out eliminates the cleaning of the boiler setting below the rear drum entirely. Soot blowers keep the heating surfaces clean as well as remove the ash deposit in the rear of the boiler.

As the author states, there can be no justification for spending a lot of money for equipment when bagasse (a by-product fuel) is used and when equipment is in service only a relatively short time during the year. These conditions always tend to slow development of furnaces or equipment capable of increasing materially the over-all efficiency of steam generation in a sugar factory. Especially, as the author states, this is true where bagasse furnishes the entire fuel requirements of the factory.

The test results of the integral-furnace boiler given in the paper are interesting, and the performance indicated therein is entirely acceptable to anyone versed in the combustion of bagasse.

M. V. Yarbrough.[7] As pointed out by the author, "green" bagasse was sun-dried before its utilization as fuel during the early days of sugar manufacture. Actually the green bagasse was not burned without predrying until about 1860. Then for the next 75 years, green bagasse was burned only in Dutch-oven-type furnaces. All during this period it was a generally accepted fact that even at considerable expense, such furnaces must be shielded completely from the "dark" boiler heating surfaces.

Only a man of vision, with imagination, fundamentally highly inquisitive, and with capacity to re-co-ordinate known facts into new ideas could possibly dare question such a well-established and generally accepted "fundamental principle." Such a man was G. P. Ward. It remained for him to suspect and finally prove that a furnace only partly shielded from dark boiler surfaces would not only burn green bagasse but also do a magnificent job of it.

The doubting Mr. Ward, highly practical "dreamer" that he was, also entertained unique ideas regarding bagasse as a fuel. For 75 years other highly trained and capable specialists had tested bagasse in the attempt to precisely evaluate green bagasse as a fuel, using methods of evaluation recognized as applicable to other fuels. While fully recognizing the value of such information, Mr. Ward, in his thinking, attached great importance to the characteristics of bagasse which cannot be precisely measured nor interpreted with respect to the burning qualities of various bagasses. These variable, and precisely indeterminable qualities which may be properly termed physical characteristics of various bagasses, otherwise apparently identical, were discussed often and at great length by Mr. Ward and the writer during many years of friendship and close association. The more experience the writer accumulates in combustion of various bagasses as the years go by, the more convinced he is that Mr. Ward was entirely correct in his belief that many factors which definitely influence the combustion of various bagasses are incapable of precise determination and interpretation.

Bagasse is a constantly variable material. It is everything from the cane stalk except the juice removed by the sugar mill. It also includes some of the juice which exists in the cells of the cane plant but not removed in the milling process. Sugar-cane stalks as to framework are composed essentially of the rind, the nodes between joints, and the pith. Proportions of these component parts of the cane stalk vary widely and are determined by the variety of cane, its cultivation and fertilization, and weather conditions prevalent during the growth of the plant, as well as the state of maturity of the cane when harvested. In all cane-producing areas, with the possible exception of irrigated areas, cane cut at the start of each season is not fully mature, and maturity proceeds as the harvest season continues.

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[7] General Manager, Young's Industries, Inc., Youngsville, La.

The amount of cane juice remaining in the bagasse, as well as its locale in the plant cells, is determined by the efficiency of the mill. The efficiency of the mill is determined by fiber-grinding rate and "millability" of the cane. Millability and fiber of the cane are determined by the proportions of rind, nodes, pith, and "hardness," or compressibility, of the mixture of rind, node, and pith cells.

Thus a sugar mill must grind sugar cane which is a constantly variable material. The sugar mill produces bagasse just as variable as the sugar cane from which it is processed.

Yet bagasse furnaces must burn either (1) all of this constantly variable fuel necessary to generate the steam being consumed, or (2) all of the bagasse being produced by the mill. Steam demands in most sugar factories peak rather frequently, and the swing from low to high steam demands is relatively great and extremely rapid.

Thus the solution of the problem of designing bagasse furnaces had to be slow. Solution of a complicated problem which can be completely composed is difficult. For the reasons cited the problem of bagasse combustion cannot, up to the present, be fully composed, and its solution has been correspondingly slow and difficult.

However, when it has become possible to design bagasse-burning furnace-boiler combinations which perform as do the units described by the author, progress has indeed been achieved. Furthermore, the rate of recent progress has been rapid.

It was approximately only 12 years ago that Mr. Ward became convinced there was something wrong with the "fundamental principle" that green bagasse furnaces had to be completely shielded. Remember, that fundamental principle was nearly 75 years old.

Rather wide experience with Ward single-pass furnaces has convinced the writer that they do perform, and with the advantages outlined by the author, on the various types of bagasse encountered from day to day and from season to season.

Thus again, as has been the case with many other industrial improvements, it appears that the solution to the problem is proceeding in advance of our ability to compose the problem completely.

E. W. Kerr.[8] During recent years there has been a more or less general increase in the fiber content of sugar cane in Louisiana; in other words, an increase in the weight of bagasse to be burned per ton of cane processed. The writer recalls that in Cuba the average for several years was 10.75 per cent on cane, while here in Louisiana it varies from, say, 12 to 15 per cent or more. In such cases the problem becomes one of consuming bagasse rather than of utilizing steam efficiently; in fact, it is not uncommon to blow steam off through the safety valves when there is a surplus. This is done even though there is a bagasse storage, because with such surplus, filling the storage is a matter of only a few hours.

Also, during the past grinding season the burning of bagasse in the furnaces was made more difficult owing to a great deal of wet weather which resulted in wet cane leaves and dirt being brought from the fields. It is common practice to burn the leaves from the cane after it is cut in the fields but of course this cannot be done in rainy weather. Also, cane is loaded in the fields with mechanical grab-type loaders. During wet weather the grabs take up a great deal of mud which reaches the furnaces and adds to the difficulty of burning. Although these conditions are abnormal they have to be taken care of when encountered.

A great many boiler trials have been made in which both bagasse and feedwater were weighed. Weighing of bagasse is rather difficult because of its volume, the most common method being to weigh it on platform scales in corn baskets. The writer was associated with Mr. Ward in making a large number of tests in which the bagasse was weighed in 1000-lb lots in a wooden box hung on a scale. These tests were made on a straight-tube water-tube boiler of 959 rated horsepower, the load varying from 85 to 155 per cent of rating, and the efficiency varying from 52 to 62 per cent. In a paper[2] by the writer, in 1939, is given results of a test by Mr. Ward on a 1290-hp Stirling-type boiler at Mercidita factory in Puerto Rico, which was carried out in 1935. The efficiency in this test was 77 per cent and is the highest figure in the writer's knowledge. The installation included an air heater with Ward-Gregory furnace (not a Ward furnace).

Referring to the Ward furnaces as illustrated in the present paper, this type of furnace is designed to enable high ratings and high efficiency without carry-over of ash, the latter being one of the objectionable features encountered with the hearth-type (standard) furnace. It may or may not have air heaters. The restricted area at the top (bottleneck) is to assist in the concentration of heat such as will aid in the combustion of remaining particles. One of the most troublesome and expensive (in labor) features in connection with our standard-type hearth furnaces is this carry-over of ash from the horseshoe over the bridge wall. This must be removed through doors in the side walls of the setting instead of the doors at the front of the hearths.

By reducing the area of the exposed setting walls the radiation loss is reduced. It would seem that, from this aspect, a straight-tube boiler with the furnace directly underneath the first pass would give the least radiation loss. In fact, the area in Fig. 2 of the paper probably has as much area for radiation as would an extension furnace of the standard horseshoe type with greater length but less height. Mr. Ward's first installation of his furnace was under such a straight-tube boiler, which gave an efficiency of 66 per cent. The radiation area appears to be much less in the Fig. 1 installation.

Considering the question of baffling, it would appear that the arrangement shown in Fig. 2 of the paper (reduced) should be in connection with an air heater in order to reduce the temperature of the gases and increase efficiency. A common height of chimneys in Louisiana factories is 175 ft which should be sufficient to take care of a furnace unit with regular boiler baffles without air heater, with good efficiency for our conditions. Of course the use of an air heater adds to efficiency as well as helps in eliminating ash carry-over, but it will involve higher cost of installation, including cost and upkeep of refractories due to high temperature. Whether or not this would be justified would depend on the length of grinding season each year which is greater in the tropics than in Louisiana. In fact, it would seem that for Louisiana a Ward furnace with regular baffling and without air heater should be sufficient, in view of the grinding season lasting only some 2 months. The grinding season in the tropics is more of the order of 4 months.

Author's Closure

As Mr. de Lorenzi points out, the original Ward furnace had a double throat to shield the burning fuel pile from the boiler tubes which were located immediately above the throat. When Ward furnaces were installed under Stirling boilers, such complete shielding was not thought necessary because the boiler tubes are located to one side of the furnace. The front half of the double-throat arrangement was eliminated in 1939 as being unnecessary. The elimination of this part of the throat arch actually improved conditions for high-rating operation because the velocity through the throat was reduced, resulting in a reduction of about 0.1 in. in draft loss and a consequent increase in steam output on natural draft.

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[8] Head, Firm of E. W. Kerr, Consulting Engineers, Baton Rouge, La. Mem. ASME.

Mr. de Lorenzi's comments on a spreader stoker in Cuba for firing bagasse is very informative and adds a new method of burning bagasse. However, this method involves burning bagasse on grates, the troublesome maintenance of which resulted in the development of the hearth or grateless type of furnaces which are so generally in use today. Only time can tell whether the grates under the spreader stoker can satisfactorily avoid the troubles due to burning, warping, and clogging experienced with the earlier designs. The thin fuel bed may be a liability in the event of insufficient bagasse feed or complete stoppage for several minutes.

When the author saw this installation, it was base-loaded by automatic control so that its behavior under the widely swinging loads, so common in sugar mills, could not be observed.

Mr. E. L. Dennis apparently also has some doubts about using grates. His comments on the high burning rates obtainable in hearth-type furnaces is quite pertinent. The burning rate on the spreader-stoker-fired job mentioned by Mr. de Lorenzi is about 80 lb per sq ft, whereas the burning rate in the Ward furnace, shown in Fig. 3, is more that 400 lb per sq ft. Mr. Dennis' comment on the harvesting of dirt with the cane during adverse weather conditions and possible difficulties in burning the bagasse is also pertinent because when these conditions exist, the steam plant must produce steam from bagasse, regardless of conditions. Mr. Dennis' comments about bagasse sizing, predrying, and burning in pulverized form are worthy of note because Mr. Dennis speaks from many years' experience.

Mr. Yarbrough brings out some of the reasons why bagasse is such a constantly varying material, differing from most other fuels in this respect. Mr. Yarbrough's comments really are a fine tribute to the memory of Mr. Ward, whom he knew so well and with whom he had so many discussions on this subject. It is unfortunate that Mr. Ward did not live to see the development of his basic idea, applied to so many furnaces all over the sugar-producing world.

It was very nice to have Professor Kerr attend this meeting and deliver some extemporaneous comments based on his many years of experience in burning bagasse. Rather than using an air heater with the low-draft-loss boiler shown in Fig. 2, the gas baffles can be arranged to provide better efficiency when draft is available as would be the case with 175-ft stacks mentioned by Professor Kerr. By increasing height of the vertical baffle behind the superheater and installing a vertical baffle down from the steam drum in front of the superheater, the effect of three-pass bafflings can be obtained. However, as stated in the paper, the primary object of this design of boiler was to provide a boiler which could generate steam at high capacity on natural draft from existing stacks in many plants which are not concerned with efficiency of fuel burning and which, as a matter of fact, have a problem of getting rid of excess fuel. For those plants where economy of fuel is a primary factor, the arrangements shown in Fig. 1 or Fig. 3 of the paper, containing air heater and forced and induced-draft fans will produce maximum efficiency.

The author is grateful to Messrs. de Lorenzi, Dennis, Yarbrough, and Kerr for contributing information from their experiences to this paper.

Experimental Combustion of Pulverized Coal at Atmospheric and Elevated Pressures

By H. R. HAZARD[1] and F. D. BUCKLEY[2]

Among the basic problems associated with the development of a gas-turbine plant to use pulverized coal are those related to the burning of the pulverized coal under gas-turbine conditions. These conditions include high heat-release rates, high excess air, high static pressures, and a wide range of variation in all operating conditions. No previous data indicating the effects of pressure on the reaction rate of pulverized coal were available at the start of this investigation, and there had been little occasion to burn pulverized coal at the high heat-release rates used in gas-turbine practice when burning liquid fuels. This paper presents results obtained in a study of the effect of pressure upon the combustion reaction, and describes tests made with four small air-cooled combustors operated at high heat-release rates and low pressure in connection with a small gas-turbine unit. The work described was sponsored by the Locomotive Development Committee of Bituminous Coal Research, Inc., under J. I. Yellott, director of research. It was one of several projects, related to the development of the coal-burning gas-turbine locomotive, which have been assigned to a number of universities and research institutions, and which have been described by Yellott in a recent paper.[3] At the present time, large-scale development work is under way both at Battelle, where full-scale atmospheric-pressure combustors are under test, and at the Dunkirk, N. Y., plant of the American Locomotive Company, where full-scale coal-preparation equipment is being operated with a $^1/_3$-scale combustor at full pressure.

A STUDY OF PRESSURE COMBUSTION

IN ORDER to determine the effect of pressure upon the combustion of pulverized coal, a series of tests was run in a furnace built for this purpose. This series included tests on three sizes of burners over a pressure range from 2 psi to 75 psi and over a firing range from 40 lb of coal per hr to 130 lb of coal per hr.

Description of Equipment

The Pressure Furnace. Fig. 1 is a view of the furnace in operation, Fig. 2 is a diagram showing construction of the pressure furnace.

The furnace was built up of three 2-ft lengths of 10-in. pipe, each length water-jacketed and lined with a molded carborundum sleeve 1 in. thick. A $1^1/_2$-in. port was placed at the center of each section for observation and sampling purposes, the ports being 1 ft, 3 ft, and 5 ft from the burner. A separate cooling-water circuit to each furnace section permitted determination of heat-absorption rates by measurements of the cooling-water temperature rise. Observation ports were provided at the burner section.

Burner Design. Three burners were used during the test series. These burners were geometrically similar in design but differed in dimensions to give equal burner-tip velocities for equal firing rates at design pressures of 2, 30, and 60 psi, respectively.

Fig. 3 shows the configuration of the burner for 2 psi and of the burner end of the furnace. The dimensions of the three burners are given in Table 1, the designations of dimensions being those used in Fig. 3.

TABLE 1 DIMENSIONS OF BURNERS

Burner No.	1	2	3
Design pressure, psi	2	30	60
Dimension A, in.	3	$1^7/_8$	$1^5/_{16}$
Dimension B, in.	5	$2^1/_4$	$1^7/_8$
Dimension C, in.	$4^1/_2$	5	$4^3/_4$
Dimension D, in.	$4^1/_2$	4	$4^1/_4$

Burners were designed to impart a spin to the secondary air. A spark-ignited hydrogen pilot burner located in the burner head was used to ignite the coal flame.

Furnace Pressure Regulation. Regulation of furnace pressure proved to be one of the most difficult problems encountered. A simple valve consisting of a cone in an orifice was first used to control furnace pressure, but, as sintered ash would gradually build up around the valve cone, then suddenly break loose, pressure fluctuations resulted even with the most careful manual control. Momentary fluctuations in coal-feed rate also caused pressure fluctuations, and, conversely, the coal-feed rate was very sensitive to pressure fluctuation. Redesign of the valve, as shown in Fig. 4, incorporating a pneumatic balancing piston, resulted in improved pressure regulation.

Feeding of Pulverized Coal. Throughout the test series, Elkhorn No. 3 coal, pulverized to 93 per cent through 200 mesh in a ball mill, was burned. Because of the high volatile and the low ash content of this coal, ignition and slagging difficulties were minimized. Table 2 gives the analyses of the coal used.

TABLE 2 ANALYSES OF ELKHORN NO. 3 COAL USED IN TESTS

Ultimate analysis, per cent		Proximate analysis, per cent	
Carbon	80.0	Volatile matter	35.0
Hydrogen	4.6	Fixed carbon	61.0
Oxygen	9.7	Ash	3.5
Nitrogen	1.5	Moisture	0.5
Sulphur	0.7	Total	100.0
Ash	3.5		
Total	100.0		

High heat value, 14,360 Btu per lb

Ash-fusion temperatures, F

Initial-deformation	2500
Softening	2650
Fluid	2700

A pressure hopper was filled with about 700 lb of pulverized coal and was subjected to furnace pressure plus a few pounds for pressure drop through the piping system. The coal was fed from this hopper into the primary-air stream by means of a

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[1] Research Engineer, Battelle Memorial Institute, Columbus, Ohio. Jun. ASME.

[2] Formerly Research Engineer, Battelle Memorial Institute; now Research Engineer with Locomotive Development Committee, Dunkirk, N. Y. Jun. ASME.

[3] "Coal-Burning Gas-Turbine Plants," by J. I. Yellott and C. F. Kottcamp, presented at the ASME Semi-Annual Meeting, Chicago, Ill., June 16–19, 1947.

Contributed by the Fuels Division and presented at the Annual Meeting, Atlantic City, N. J., December 1–5, 1947, of The American Society of Mechanical Engineers.

Note: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society. Paper No. 47—A-117.

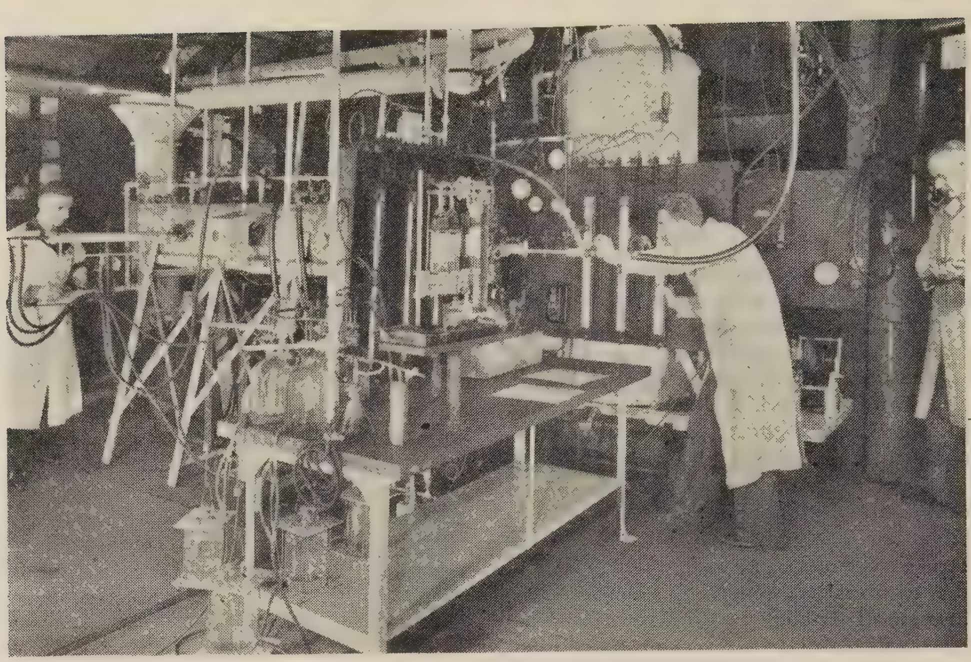

Fig. 1 The Pressure Furnace

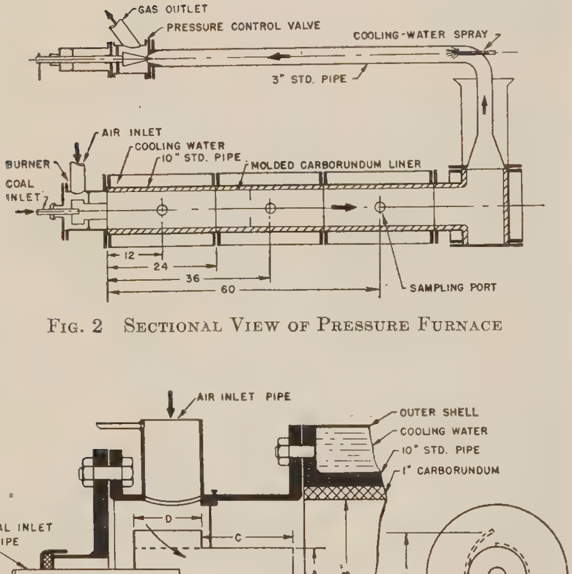

Fig. 2 Sectional View of Pressure Furnace

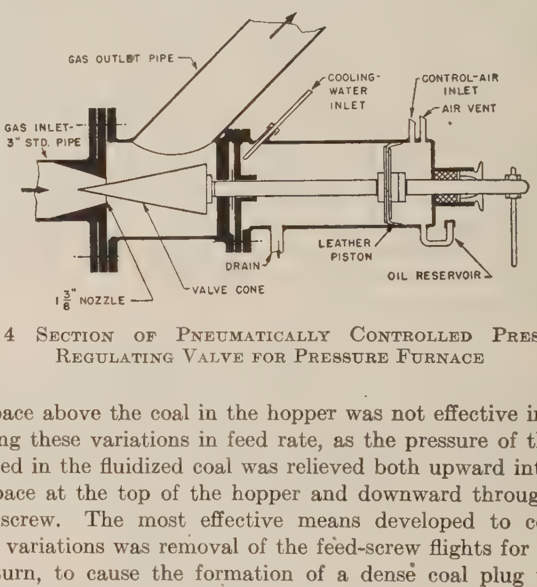

Fig. 4 Section of Pneumatically Controlled Pressure-Regulating Valve for Pressure Furnace

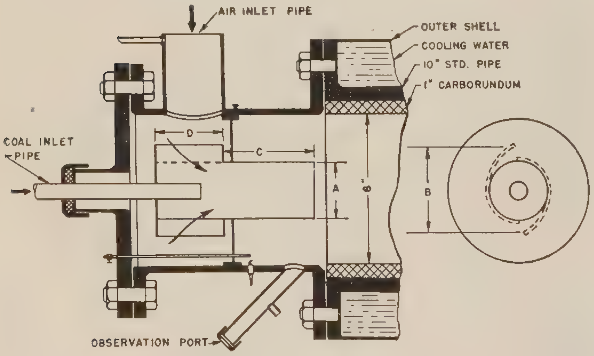

Fig. 3 Section of Burner for Pressure Furnace

variable-speed feed screw and was carried to the burner through $^3/_4$-in. piping and rubber hose. The feeding equipment was placed on a platform scale for measurement of the coal-feed rate.

Difficulty was experienced in maintaining a uniform rate of feed, as coal would surge through the feed screw upon a momentary decrease in furnace pressure, or be retarded by air blowing back into the hopper upon a rise in furnace pressure. Equalization of the air pressures between the end of the feed screw and the air space above the coal in the hopper was not effective in preventing these variations in feed rate, as the pressure of the air trapped in the fluidized coal was relieved both upward into the air space at the top of the hopper and downward through the feed screw. The most effective means developed to control these variations was removal of the feed-screw flights for about one turn, to cause the formation of a dense coal plug which would seal against a few pounds of pressure differential. It appears that a uniform coal feed may be obtained either by use of a coal feeder which seals positively against a few pounds of pressure differential across the feeder, or by some means of insuring against the occurrence of such a differential when combustor pressure fluctuates.

Air Preheater. To explore the effects of air preheat, a gas-fired preheater was used to heat the secondary air to 600 F. This preheater was of the tubular type, with high-pressure air passing through the tubes in three passes and hot combustion gases passing over the tubes in three passes.

Instrumentation of the Pressure Furnace

Gas samples were taken simultaneously through three water-cooled samplers inserted into the three sampling ports. Samples were taken at the axis of the furnace only, each sample being withdrawn at a constant rate over a period of 15 min and collected over brine for immediate Orsat analysis. Simultaneous sampling at the three locations insured identical combustion conditions for each set of samples. From each of these samples, the completeness of combustion was determined.

The rates of primary- and secondary-air flow were measured separately by means of sharp-edged orifices.

The rate of coal flow was measured by timing the intervals required to feed 5-lb increments of coal into the furnace. A mercury-switch device actuated by the scale beam gave accurate indication of the end of each time interval. From these data, variations in coal-feed rate were detected and the coal feed was adjusted to maintain a nearly constant rate.

Operating Procedure

The pressure furnace was preheated with natural gas, following which coal was fired for about an hour to stabilize temperatures, pressures, and coal rate before test data were taken.

During the test period, data were taken periodically, and gas samples were drawn simultaneously from the three furnace sampling ports for immediate analysis.

Analysis of Pressure-Furnace Data

A total of 103 tests were run at pressures of 2, 30, 60, and 75 psi, and at coal rates from 40 to 130 lb per hr. Data from tests Nos. 1 to 50 were rather erratic and were not included in correlations. Of the tests included, 19 were run with air preheated to 600 F, and 34 were run without preheat, with air at 100 F.

Data from the pressure furnace were plotted in terms of the percentage combustible burned against the residence time of the particles. The percentage combustible burned was calculated from the measured coal and air rates, and Orsat gas analyses. Three determinations were made for each test, one for each of the three sampling points.

The residence time, or time for the furnace gas to travel from the burner to the point of measurement, was calculated using measured flow rates and pressure with an assumed gas temperature of 2500 F. This calculation involves some indeterminate error in so far as the rates of burning and cooling affect the gas temperature and quantity. Necessarily, it was assumed that the residence times of the gas and particles were the same.

Figs. 5, 6, and 7 show the relation between residence time and percentage of combustible burned.

Fig. 5 shows data from tests using burner No. 1. Combustion was poor and test data rather erratic when using burner No. 1, probably owing to ineffective turbulence at the burner. A distinct improvement in combustion with increasing pressure was found for this burner, though such improvement was not evident for other burners.

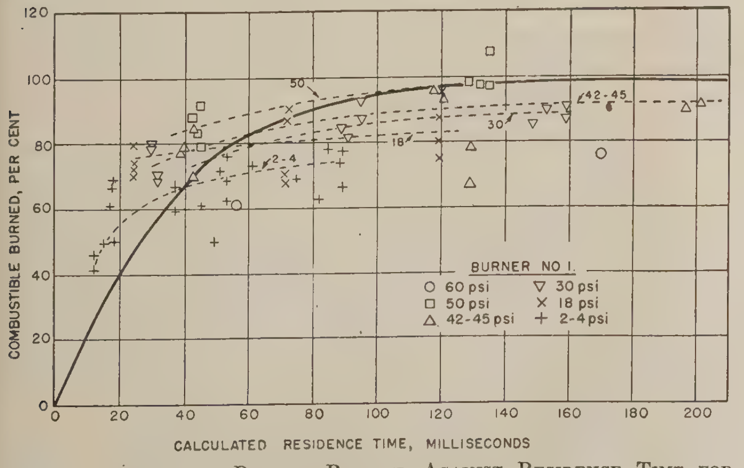

Fig. 5 Combustible Burned Plotted Against Residence Time for Burner No. 1

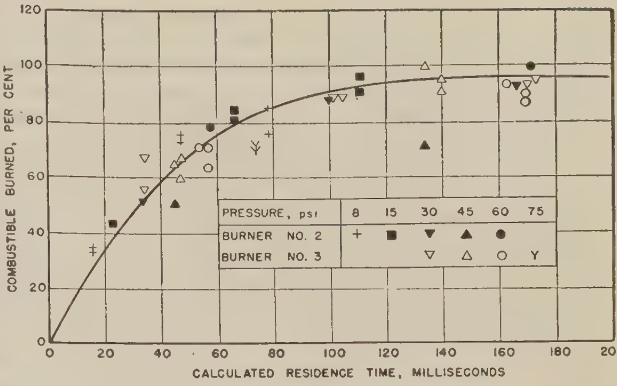

Fig. 6 Combustible Burned Plotted Against Residence Time for Burners Nos. 2 and 3

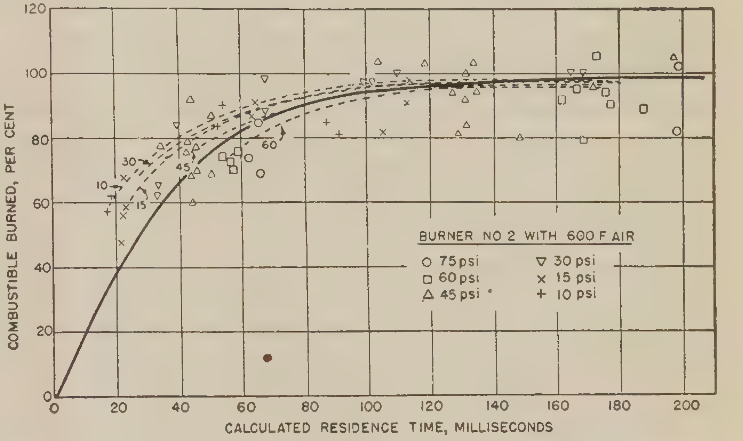

Fig. 7 Combustible Burned Plotted Against Residence Time for Burner No. 2 With Preheated Air at 600 F

Fig. 6 shows data from tests using burner No. 2 and burner No. 3 without preheat. Data obtained with these burners were less erratic than those with burner No. 1 shown in Fig. 5, and combustion was considerably better. No effect of pressure upon combustion is evident from these data.

In Fig. 7 data from tests using air preheated to 600 F with burner No. 2 are plotted. It is possible to draw a family of curves through the data points, as shown by dotted lines. From these curves it might appear that pressure affects combustion adversely to a small degree. However, it is probable that this apparent effect is an artificial result of the method of calculating residence time. For a given residence time, a high pressure represents a high firing rate and a consequent high gas temperature, resulting in increased gas volume and a consequent true residence time shorter than the calculated residence time; conversely, a low pressure represents a low firing rate, with a consequent true residence time greater than the calculated residence time. If proper correction could be made to obtain true residence time, it is probable that all points would be displaced to the heavy curve shown. Thus it is probable that for the data in Fig. 7 the effect of pressure on the combustion reaction is negligible.

The most important effect of air preheat was to improve ignition and flame stability. Without air preheat, during high-rate tests with the smaller burners, it was not unusual for the flame to burn several inches from the burner. With air preheat, as indicated both by observation and by the data in Fig. 9, the flame burned closer to the burner, giving better combustion up to the first sampling point at the higher burner velocities. From comparison of the average curves in Figs. 6 and 7, it is evident that there is little, if any, effect of air preheat on combustion over longer burning periods.

Most of the test points shown in Figs. 5, 6, and 7 were obtained at coal rates of about 130 lb per hr and with a nominal excess air of 20 per cent.

The scatter of data was believed to be caused by stratification in the furnace and by instantaneous variations of the coal-feed rate.

Conclusions From Pressure-Furnace Tests

From the data obtained from the pressure furnace, it may be concluded that the combustion reactions are not affected measurably by pressure up to 75 psi or by air preheat up to 600 F.

While the method used for obtaining and correlating data on pressure combustion was not conducive to the highest accuracy and could not be expected to define small variations in reaction rate caused by pressure, the data prove that such variations are small if they exist. For the intended purpose of providing a basis for design of pressure combustors, more elaborate work would not be justified.

It is not recommended that the curves of combustible burned plotted against residence time be used for design purposes. These curves depend upon combustor size and other variables, and are presented for comparison of data only. It appears that existing data such as those of Sherman,[4] defining the reaction rates of coals of various compositions and size consists, can be used with confidence in designing equipment for combustion at elevated pressures.

STUDY OF SMALL-SCALE GAS-TURBINE COMBUSTORS FOR BURNING PULVERIZED COAL

Concurrent with the study of pressurized combustion, a study of coal-burning gas-turbine combustors was undertaken. Of the designs considered, those which seemed to merit study were the balanced-vortex combustor, which had been the subject of an experimental investigation by Hurley,[5] and the various tubular designs characterized by combustion within a flame tube with the proper amount of air for best combustion.

An aircraft turbosupercharger was set up as an open-cycle gas turbine and was used to test four small combustors, including one of the balanced-vortex type and three of the tubular type. These combustors were built of sheet metal and were designed for high heat-release rates and low exit-gas temperatures, with air cooling throughout. The test unit, which first operated successfully in June, 1946, is believed to have been the first coal-fired gas-turbine unit to be operated in this country.

The Turbosupercharger Bootstrap Unit

The aircraft-type turbosupercharger combines two of the basic elements of the gas-turbine engine, the compressor, and the turbine. With the addition of a combustor to heat the air between the compressor outlet and the turbine inlet, a simple open-cycle gas-turbine engine is completed. This arrangement is frequently referred to as a turbosupercharger "bootstrap" unit.

The turbine was started by means of a compressed-air jet from a nozzle directed at the back of the turbine blades. At a turbine speed of about 3000 rpm, with a moderate air flow established through the combustor, a hydrogen pilot flame in the combustor was lighted and the coal feeder started. On ignition of incoming fuel, the turbine would accelerate to a speed depending on the fuel rate. The desired fuel rate was then established. As the desired combustor-outlet temperature was usually below the characteristic operating temperature of the bootstrap unit, air was supplied to the starting nozzle to increase turbine speed and the related air rate, and thus reduce turbine-inlet temperature.

Because the compressor was the only load on the turbine, any variation in fuel-feed rate caused an immediate change in turbine speed, altering all test conditions. It was thus essential to obtain a uniform feed of pulverized coal to the combustor in order to maintain constant test conditions.

The Balanced-Vortex Combustor

The balanced-vortex combustor is a design in which the forces on coal particles injected into a fluid vortex are utilized to promote combustion. In this design, combustion air enters tangentially through vanes around the periphery of a squat cylindrical chamber having a central outlet. Into the vortex thus established pulverized coal is injected. The inward flow of air toward the combustor outlet exerts a viscous-drag force on the coal particles which is approximated by Stokes' law. This force is opposed by centrifugal force due to the high rotational velocity of the particles in the vortex. By adjustment of the two vortex velocity components, it is possible to cause a particle of a given size to rotate temporarily in a circular path of any selected radius, at which time the viscous and centrifugal forces acting on the particle will be in balance.

In designing a combustor utilizing this principle, the vortex velocities may be adjusted to retain a very small particle, say, 30 microns, at the combustor-outlet diameter. Then all larger particles would be retained in the combustor by centrifugal force until they burned to the escape size. Smaller particles would pass through the combustor, with some turbulence due to the centrifugal force.

The balanced-vortex design is particularly adapted to the burning of coarser consists of pulverized coal, as coarse material would be more likely to burn in such a combustor, where it would be retained, than in a tubular design, through which it could pass without burning.

A mathematical treatment of the balanced-vortex combustor is somewhat beyond the scope of this paper. However, a limited discussion of the design has been published by Hurley,[5] and a more complete treatment, including effects of swelling of the particle, gas-temperature rise, and change of combustor cross section, has been prepared by Bell.[6]

Fig. 8 shows combustor No. 1, which was designed to burn 275 lb of coal per hr with 150 lb of air per min at 15 psi. The corresponding combustor-outlet temperature was 1600 F and the combustor heat-release rate was 3,000,000 Btu per (cu ft) (hr). The combustor consisted of a type 321 stainless liner within a sheet-steel interliner, forming a plenum chamber around the liner, and in turn enclosed in a pressure-retaining shell. The stainless liner was made in the form of a cylinder 20 in. in diam × 8 in. high. The sides of the liner were formed of eight overlapping circumferential vanes having an opening between vanes of approximately $^1/_4$ in. The bottom was conical in shape, covered by $^{1}/_{2}$ in. of plastic chrome ore to aid ignition, and had a $6^{1}/_{2}$-in-diam center outlet. The top was flat. All of the air entered the combustor tangentially from the plenum chamber between the combustor liner and the interliner, which were spaced to maintain high air velocity over all parts of the liner. The top of the liner was cooled by air passing radially inward to a 3-in. hole at the center. The circumferential vanes were cooled by combustion air in the plenum section, and the bottom was cooled by the bulk of the excess air. The liner and interliner were supported from the cover of the outer shell, the whole assembly being removable from the outer shell as a unit. Pulverized coal was injected through 6 nozzles equally spaced on a 14-in-diam circle in the top of the combustor. The coal was ignited by means of a small spark-ignited hydrogen torch in the top of the combustor. Five sighting ports were placed to allow observation of the flame. A coke separator, utilizing the swirl of the combustor exhaust gas, was attached to the combustor outlet to protect the turbine from damage.

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[4] "Burning Characteristics of Pulverized Coals and Radiation From Their Flames," by R. A. Sherman, Trans. ASME, vol. 56, 1934, p. 401.

[5] "Some Factors Affecting the Design of a Small Combustion Chamber for Pulverized Fuel," by T. F. Hurley, *Journal of the Institute of Fuel* (British), vol. 4, 1931, pp. 243–254.

[6] "Motion in a Balanced-Vortex Combustor," by J. C. Bell, Appendix of Eighth Progress Report by Battelle to Locomotive Development Committee on "Combustion of Pulverized Coal for Gas-Turbine-Driven Locomotive," May, 1947.

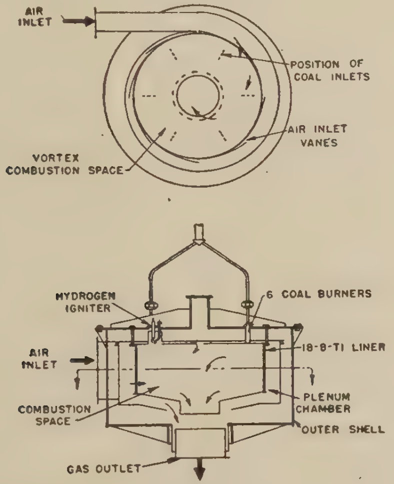

FIG. 8 COMBUSTOR NO. 1, THE BALANCED-VORTEX COMBUSTOR

Combustor No. 1 was built for a brief trial to determine the suitability of such a design for gas-turbine application. No provision was made for measuring or controlling the division of combustion air and cooling air so that actual combustion conditions could be studied. The combustion-air vanes were merely adjusted to give the best combustion conditions and a few tests were run to observe the effects of coal fineness and firing rate. Following these tests, work on the balanced-vortex combustor was suspended, and similar tests were run on tubular combustors to permit comparison of operating characteristics.

Arrangement of Test Equipment. Fig. 9 shows the arrangement of equipment used for testing combustor No. 1. Air enters the turbosupercharger compressor (2) where it is compressed to a pressure of from 2 to 12 psi, depending upon speed and therefore upon firing rate. From the compressor outlet it goes to the combustor (4) where it is heated by the burning of the coal. The heated air from the combustor goes through a cyclone separator (6), which removes any large agglomeration of coke, which might damage the turbine. After passing through the turbine (9), the air is exhausted to the atmosphere through a short straight stack. The flow of primary air carrying the pulverized coal in suspension is controlled by a valve at the combustor (5), and the coal rate is controlled by variation of the speed of the coal feeder. Coke can be removed from the cyclone by removing a cap (7) at the bottom of the cyclone. The turbine is started by means of a compressed-air jet directed at the exhaust side of the turbine blades (12).

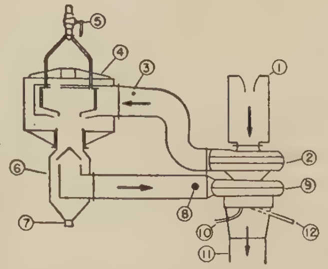

FIG. 9 ARRANGEMENT OF EQUIPMENT USED TO TEST THE BALANCED-VORTEX COMBUSTOR

In order to make a heat balance, it was necessary to measure coal rate, primary-air rate, compressor-inlet air rate, combustor-inlet temperature, and combustor-outlet temperature. Compressor air rate was measured by a $4^{3}/_{4}$-in. elliptical flow nozzle (1), Fig. 9, for which ASME coefficients were available. Combustor-inlet temperature was measured by a chromel-alumel thermocouple in the air duct (3). Combustor-outlet temperature was measured with a quadruple-shielded, 22-gage chromel-alumel thermocouple, located at the turbine inlet (8). The temperature gradient across the pipe was less than 10 F at this point owing to the excellent mixing obtained in the cyclone (6). A single-point high-speed electronic recorder was attached to this thermocouple, allowing close observation of temperature variations and close determination of mean gas temperature from the chart.

As a check on the heat-balance method of determining combustion efficiency, an ash balance was also made. Exhaust gas was sampled by a $^{3}/_{4}$-in-diam sampling tube placed $^{1}/_{8}$ in. from the discharge side of the turbine blades (12), Fig. 9. The sample was aspirated through a flannel bag which removed the fly ash. The sample velocity entering the sampling tip was held approximately the same as the velocity of the surrounding exhaust gas. As the coke cyclone removed nothing but larger agglomerations of coke sometimes formed in lighting off the combustor, it did not interfere with the accuracy of the ash balance.

Coal Preparation, Feeding, and Measurement. Fig. 10 is a Bennett[7] diagram on which sieve analyses for the coal burned during all combustion tests are plotted. Elkhorn No. 3 coal was burned during all tests. The coal was pulverized to 85 per cent through 200 mesh, and 93 per cent through 200 mesh for tests on combustor No. 1.

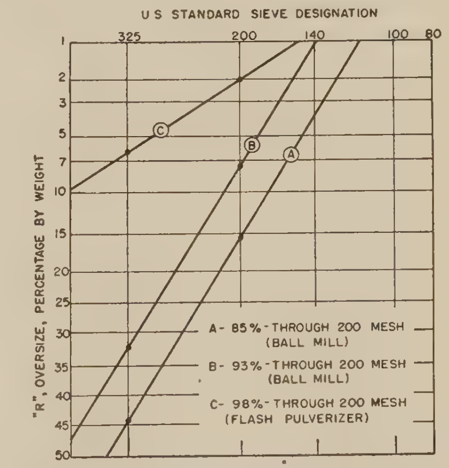

FIG. 10 BENNETT DIAGRAM SHOWING SIZE CONSISTS OF PULVERIZED COAL USED IN COMBUSTOR TESTS

Coal was fed to the combustor by means of a commercial screw feeder fitted with a pressure hopper and operated at about 20 psi. The coal rate was measured by placing the entire feeder on scales and checking the weight loss at 5-minute intervals.

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[7] "Broken Coal," by J. G. Bennett, *Journal of the Institute of Fuel*, vol. 10, 1936, pp. 22-39.

The instantaneous rate of coal feed was indicated by a BCR air-coal flowmeter.[8] This meter was very sensitive to changes in coal rate, immediately indicating any irregular coal-feeding conditions. As most of the early operating difficulties were traced to variations in the coal-flow rate, the meter proved to be an invaluable operating aid. As integration of the meter indication of coal rate was less accurate than periodic weight checks, the latter were used for heat-balance calculations.

Description of Operation

Following preliminary operation to adjust the combustor for satisfactory operation, a series of 9 tests were run on combustor No. 1. This series included tests at high release rates of 2.3 to 2.9 million Btu per (cu ft) (hr) and at a low rate of 1.5 million Btu per (cu ft) (hr), burning both coarse coal (85 per cent through 200 mesh) and fine coal (93 per cent through 200 mesh). A final test was run with the refractory removed from the bottom of the combustor.

The flame during all tests was cylindrical in shape with a diameter of about 12 in. It extended from the combustor outlet to the cone of the coke separator, where it was quenched by the cooling air. At low rates, a flame temperature of 2700 F was measured with an optical pyrometer; at high rates pyrex sight glasses melted and pyrometer data could not be obtained.

A thin layer of fluid slag formed over the surface of the refractory floor, but no other ash accumulations formed. With the refractory removed, no slag was deposited in the combustor during a single test.

Large pieces of coke were sometimes formed when lighting proved difficult. These usually revolved around the outside of the combustor until burned, though some escaped, to be caught in the coke separator.

The combustor proved quite stable as long as a flame temperature above 2700 F was maintained. At lower flame temperatures, combustion was unstable.

Lighting off required a rich mixture at the igniter, obtained by firing an excess of coal for the reduced air rate available at starting.

Gas samples taken from the turbine inlet contained no CO. The entire combustion loss was in the form of unburned carbon.

Thermocouples placed at 10 points on the stainless liner indicated moderate metal temperatures at all points except the center of the top plate, which reached 1430 F. This temperature could have been reduced by passing more cooling air over the top plate.

Excellent test conditions were maintained throughout the test series. Combustor-outlet temperature, the variable most sensitive to variations in coal feed, was held constant within ± 20 F through most of the tests.

No reliable data on pressure loss were taken. However, calculations indicate that pressure loss should be similar to that for other types of gas-turbine combustors currently in use. This was substantiated by the excellent operation of the turbosupercharger bootstrap unit, which will not operate at all unless pressure loss is small.

Combustion Efficiency. Combustion efficiency was determined for each test by a heat balance based upon measured flow rates and temperatures. As a check on the heat balance, an ash balance was also made for each test. The percentage of ash in the coal and the percentage of combustible in the stack-dust sample were determined by laboratory analysis. On the assumptions that the ash weight was not changed in the combustion process and that all the ash left the combustor as fly ash, the weight of unburned carbon per pound of coal was determined.

In view of the simple instrumentation used, the agreement between heat-balance efficiencies and ash-balance efficiences was good; the average variation between values amounted to about 3 per cent.

In Fig. 11 combustion efficiency is plotted against residence time for all tests on combustor No. 1. Residence time was calculated as the ratio of combustor volume to volume per second of air passing through the combustion space. The air volume was calculated for an average temperature of 2700 F and for the static pressure measured for each test. This residence time is that for the air passing through the combustor, and does not necessarily apply to the coal particles. As the flame occupied only a 12-in-diam cylinder at the center of the 20-in-diam chamber, the true time available for combustion was about one half of the total calculated residence time.

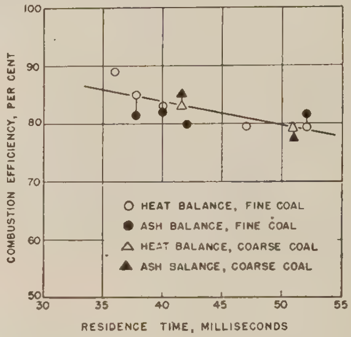

Fig. 11 Combustion Efficiency Plotted Against Air Residence Time for Balanced-Vortex Combustor

Fig. 11 points out the oustanding characteristic of the vortex combustor, that the combustion efficiency increases with an increase in firing rate and consequent decrease in residence time, as compared to a decrease in combustion efficiency expected in a tubular combustor. There are two factors acting to improve combustion at higher rates: (*a*) higher flame temperature improves ignition and flame stability; (*b*) a change in the force balance increases the ratio of outward centrifugal force to inward viscous-drag force, resulting in a decrease in particle escape size.

Conclusions From Tests on Balanced-Vortex Combustor. From brief tests on an improvised design of balanced-vortex combustor, it appears that such a combustor can be built to operate under gas-turbine conditions. This design might prove to be a means of burning coal at much higher heat-release rates than would be economical in tubular combustors, as coal particles can be retained in the combustor for a much longer time than the air passing through. However, development is necessary to improve ignition and turndown characteristics before such application can be made.

Tubular Combustors

Arrangement of Test Equipment. Combustors Nos. 2, 3, and 4 were tubular combustors, which were merely interchanged in the turbosupercharger duct work, with no change in operating procedure or instrumentation. The test equipment was essentially the same as that used to test the balanced-vortex combustor, though the coke separator was removed, the duct work rearranged and the measurement points relocated.

Combustion efficiencies were determined both by heat balance and by ash balance. For the ash balance, a sample was taken from the center of the exhaust pipe 8 in. from the combustor outlet. The sampler was a $^1/_2$-in. stainless-steel tube with a scoop formed at the end, facing upstream. From the sampler the gas passed successively through a water-cooled heat exchanger, a small cyclone to remove burning coke particles which could not be contained in a cloth bag, and an 8-oz Canton-flannel bag filter. As the pipe was under several pounds of pressure, no aspiration was necessary. The resistance of the heat exchanger gave the proper sampling velocity at an average pressure. No means was provided for adjusting sampling velocities. The combustor-outlet temperature was measured by a quadruple-shielded chromel-alumel thermocouple placed 8 ft from the combustor outlet. This distance was sufficient to minimize the effect of stratification at the combustor outlet. The combustor pressure loss as measured included the loss in two 90-deg bends. The highest calculated bend loss was only 0.20 in. of water, so that the error involved in this determination was negligible.

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[8] "Meter for Flowing Mixtures of Air and Pulverized Coal," by H. M. Carlson, P. M. Frazier, and R. B. Engdahl, Trans. ASME, vol. 70, February, 1948, pp. 65–79.

Preparation of Pulverized Coal. During tests on tubular combustors, Elkhorn No. 3 coal was burned. This was pulverized to 85 per cent through 200 mesh and 93 per cent through 200 mesh, using a ball mill. A "superfine" product was prepared by passing coal mechanically pulverized to 85 per cent through 200 mesh through a flash pulverizer to reduce it to 98 per cent through 200 mesh. The size consists for these three degrees of pulverization are plotted in Fig. 10.

The flash pulverizer, or coal atomizer, is a development of J. I. Yellott. Its design includes a pressurized hopper in which crushed coal is stored, a device to feed coal from this hopper into a stream of primary air at the same pressure, and a critical-flow nozzle, followed by an attrition device. Pulverization is obtained both in the nozzle and in the attrition device. The equipment used for these tests includes a pressure hopper of 500 lb capacity, a feed screw rotating at speeds from 40 to 200 rpm, a ¼-in. critical-flow nozzle, and an attrition chamber consisting of a 10-in-diam cone, the nozzle discharging tangentially into the base of the cone and the pulverized coal leaving through a 1¼-in. pipe at the apex. A flash-pulverizer air rate of 350 lb per hr at 80 psi was used.

COMBUSTOR NO. 2

Fig. 12 is a sectional view of combustor No. 2. This combustor was a standard unit manufactured for the General Electric TG-180 jet engine, and was designed to burn liquid fuels. The only modifications made for coal-burning tests were: (*a*) removal of the ignition tubes provided for connection to other combustors; (*b*) substitution of a hydrogen ignition for a spark plug; and (*c*) addition of observation ports and piping flanges.

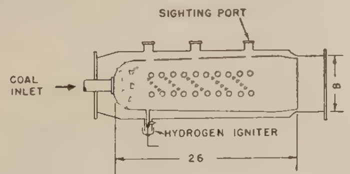

FIG. 12 COMBUSTOR NO. 2, A MODIFIED TG-180 JET-ENGINE COMBUSTOR

The combustor consisted of an outer shell, a perforated cylindrical flame tube with a hemispherical head, an igniter, and an inlet for primary air and coal. The flame-tube perforations consisted of 10 rings of 8 holes spaced equally and arranged in rows. Between these holes, 120 slots were placed in a spiral pattern to admit air to sweep the entire inside surface of the flame tube. The hemispherical head of the tube had a pattern of slots arranged to sweep the entire surface. An annular space at the exhaust end of the flame tube allowed some of the air to pass over the tube without entering any of the perforations. Distribution of area for flow, which is the approximate distribution of flow through the various perforations was such that 75 per cent of the air entered the 80 large holes. The igniter used was a small hydrogen burner which was lighted with a spark plug. It was placed, as shown in Fig. 12, to ignite the rich air-fuel mixture in the hemispherical flame-tube head.

The inlet for primary air and coal was made from a piece of 1¼-in. pipe machined to fit into the hole provided for an oil atomizer. In this pipe was placed a spreader consisting of eight radial vanes, curved at the outlet end, which deflected the eight coal streams from the tip to give a dispersion in the form of a hollow-cone spray having an included angle of about 90 deg. The spacing of these vanes was somewhat unsymmetrical, causing nonuniform coal distribution. Three of the heavier coal streams impinged upon the flame tube, causing coke depositions.

Tests on Combustor No. 2. Thirteen tests were run on combustor No. 2 to explore the effects of coal fineness, firing rate, and temperature rise on combustion. Four of these tests were run at coal rates of about 160 lb per hr, and nine were run at coal rates of about 70 lb per hr. The corresponding heat-release rates were 2.5 million Btu per (cu ft)(hr) and 1.25 million Btu per (cu ft)(hr), respectively. Comparison of plots of combustion efficiency against the several variables involved led to the conclusion that the primary variables, at least for the high combustion rates studied, were the time allowed for combustion and the coal fineness. Residence time was calculated as the ratio of combustor volume to volume per second of air through the combustor, using an average temperature and air weight calculated for the mid-point of the combustor for each test.

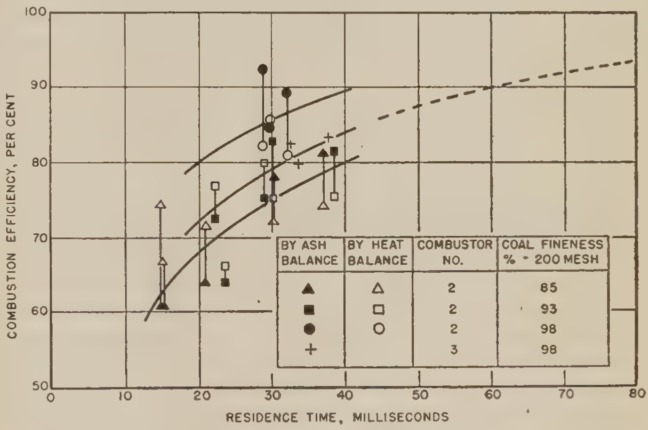

FIG. 13 COMBUSTION EFFICIENCY PLOTTED AGAINST RESIDENCE TIME FOR COMBUSTORS NOS. 2 AND 3

In Fig. 13 combustion efficiency is plotted against residence time, with data points from all tests on combustor No. 2 shown. The bottom curve represents combustion of the coarsest coal (85 per cent through 200 mesh), the intermediate curve represents combustion of the finer coal (93 per cent through 200 mesh), and the highest curve represents combustion of the finest coal (98 per cent through 200 mesh). Although the small number of test points does not accurately determine the position of these curves, it is evident that coal fineness has a marked effect on combustion efficiency when combustion time is severely limited. The dotted curve is taken from Sherman's data, and represents data from a large refractory furnace burning similar coal pulverized to 80 per cent through 200 mesh. It is evident that somewhat lower efficiency was obtained in the test combustor burning coarse coal than would be indicated by Sherman's data. This difference is probably due to the high radiation loss from the flame in the small combustor.

Ignition characteristics of this combustor were excellent under all conditions. The arrangement of flame-tube perforations was such as to give air/fuel ratios ranging from 2.5 to 8.5 at the igniter as the combustor air/fuel ratio was varied from 30 to 70, with corresponding outlet-gas temperatures of 1700 F to 900 F. No pilot flame was required, and the flame was stable with combustor outlet temperatures as low as 600 F, the lowest temperature tested.

The conical spray of coal from the burner impinged upon the flame tube owing to unsymmetrical coal distribution, with the result that deposits of coke were formed in the head of the combustor. This condition was most troublesome at the highest firing rates, when large pieces of coke broke loose periodically to blow downstream to the turbine. At the firing rate of about 70 lb per hr used for most of the tests, only a small amount of coke collected in the head. This built up to an equilibrium thickness of about $^1/_2$ in. over a small area, and burned away at about the same rate as fresh coal was being deposited. Small pellets of burning coke having diameters of $^1/_8$ in. or less broke loose in a continuous hail, and continued to burn through the turbine and stack. It was felt that the impingement of coal on the flame tube was due largely to poor distribution of coal and primary air and that such a condition could readily be remedied in larger equipment.

The low pressure drop for this combustor indicated that a satisfactory degree of turbulence may be obtained in a small combustor with little pressure loss.

The combustor was provided with five sighting ports through which the flame and flame tube could be observed. At the burner end of the flame tube, the combustion was intense, the outer shell reaching red heat opposite the first two rows of holes during all tests. The flame was opaque and incandescent at this end, with a flame temperature of about 2700 F, as measured by an optical pyrometer.

Examination of the combustor after about 20 hr of intermittent testing revealed an irregular deposit of fine sintered ash about $^1/_{64}$ in. thick over the entire inner surface of the flame tube. This deposit was a light reddish brown in color and rubbed off very easily. Slagging was not expected in this combustor because the small size resulted in comparatively low flame temperature, and because the walls were completely swept by air entering through regularly spaced slots.

It appears that the jet-engine type of combustor has several advantages, including simple construction, ease of ignition under a wide range of conditions, stable combustion under all conditions, relatively low presssure drop, and freedom from slagging. It is inherently a wide-range combustor, permitting satisfactory operation over the range of combustor-outlet temperatures required for gas-turbine service.

COMBUSTOR No. 3

The essential details of combustor No. 3 are shown in Fig. 14. This combustor consisted of an unperforated flame tube fired by a scaled-down model of a conventional design of circular burner used in firing boilers. This flame tube was $7^1/_2$ in. in diam × 23 in. long, and was placed in the outer shell of combustor No. 2.

Primary air and coal entered through a $1^1/_4$-in. pipe. A spiral-vaned spreader in this pipe formed a hollow-cone spray as the coal left the burner. Secondary air entered around the coal pipe through a $2^1/_8$-in. throat. Six peripheral vanes imparted a spin to the secondary air in the same direction as the spin of the primary air. The total amount of air entering at the burner was estimated to vary from 130 to 200 per cent of theoretical combustion air over the range of combustor-outlet temperatures tested. Remaining air passed around the flame tube to mix with the gas at the downstream end. The igniter was the same as was used with combustor No. 3, and its position was not changed.

Tests on Combustor No. 3. Only three tests were run on combustor No. 3, as it was obvious that alterations were needed, and the outer shell, taken from combustor No. 2, was unsuitable for these alterations. The combustion efficiency during these three tests appeared to be about 5 per cent below that obtained with combustor No. 2 under similar conditions. Points representing these tests are plotted in Fig. 13.

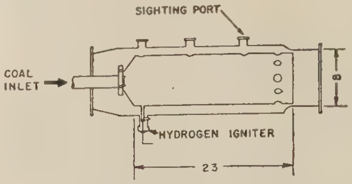

FIG. 14 COMBUSTOR No. 3

Ignition was unsatisfactory, as it was impossible to light the combustor at normal air-flow rates. Once ignition was established, the flame was stable over a satisfactory range of operation, and no pilot flame was required for continued operation. It was felt that this was due to the location of the igniter in a zone of lean mixture, in contrast to combustor No. 2 for which the igniter was located in a zone of rich mixture.

Pressure drop was relatively high in combustor No. 3, at 8 in. of water. This was due to excessive restriction of air flow at the burner and could probably be reduced greatly with little change in combustion characteristic.

The outer shell of combustor No. 3 operated at red heat over its entire length.

A thin coating of fine sintered ash was found on the inside of the flame tube. Coke was deposited in the burner head in a similar manner to that found in combustor No. 2.

COMBUSTOR No. 4

Results from combustors Nos. 2 and 3 seemed to indicate that the short time allowed for combustion placed a limitation upon combustion efficiency. Accordingly, combustor No. 4 was made considerably larger than the previous combustors so that a higher range of residence time could be explored.

Fig. 15 is a sectional view of combustor No. 4. This combustor was designed to burn 50 lb of coal per hr at a heat-release rate of 275,000 Btu per (cu ft)(hr), with a corresponding particle residence time of 150 millisec.

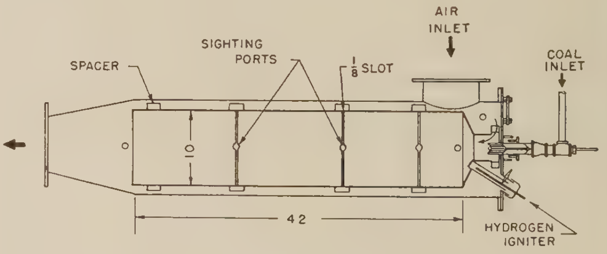

FIG. 15 COMBUSTOR No. 4

The combustor consisted of a 10-in-diameter flame tube 42 in. long, a circular burner, a hydrogen igniter, and an outer shell. The flame tube was made of four short cylinders placed end to end, with $^1/_8$-in. slots between the ends of adjacent cylinders to admit a film of air over the inside wall surface. The burner was similar to that used in combustor No. 3, incorporating the same coal distributor in a circular burner. The tube admitting secondary air was 2 in. diam and 3 in. long. With the coal distributor extending out of this throat slightly, a conical dispersion of primary air and coal, surrounded by secondary air, was obtained. Retracting the coal distributor to the rear of this throat resulted in premixing of the coal and secondary air before ignition. The hydrogen igniter was so placed that a small flame was directed into the rich mixture leaving the tip of the coal distributor. Seven sighting ports were placed to allow visual observation of combustion conditions and of metal temperatures throughout the flame tube.

Tests on Combustor No. 4. During two tests run on combustor

No. 4 at its design rate of 50 lb of coal per hr, Elkhorn No. 3 coal, pulverized to 93 per cent through 200 mesh, was burned. The first test was run with the fuel distributor flush with the inside of the flame-tube head, and the second was run with the fuel distributor retracted 2 in. into the burner throat, causing premixing of coal and secondary air before ignition. This change caused no apparent difference in the performance of the combustor. At a residence time of 144 millisec, combustion efficiency obtained was 85 per cent.

The performance characteristics of combustor No. 4 were excellent. Quick positive ignition was obtained at normal operating air rates, the flame was stable at outlet temperatures as low as 700 F, and no pilot flame was required during operation.

During operation, the burner head of the flame tube was heated to a visible red color; the remainder of the flame tube was not heated visibly. The visible combustion, or flame luminosity, ended about 18 in. from the burner. Large particles which were visible at this location passed through the remaining 24 in. of combustion space with little change in appearance. The hottest observable portion of the flame was immediately adjacent to the burner, at 2500 F, with flame temperature falling rapidly in the first 6 in. of combustion space.

No coke deposits of any kind were formed during operation at the design rate. At higher firing rates, with a deficiency of air at the burner, heavy coke deposits could be formed over the entire flame-tube head up to the first peripheral air slot.

Inspection of the combustor after tests revealed a much greater ash accumulation than had been found in previous combustors. The inside of the flame-tube head, up to the first peripheral air slot, was covered to a depth of $^3/_{32}$ in. with fused slag. The remaining 36 in. of the flame-tube length was coated to a uniform thickness of about $^3/_{32}$ in. by an extremely fine, flourlike coating of ash from which the carbon had been completely burned. It is suspected that the low gas velocity through this flame tube, about 30 fps, was a contributing factor to this ash accumulation.

CONCLUSIONS FROM TESTS ON TUBULAR COMBUSTORS

From the few tests run on two types of small tubular combustors, it is evident that combustion of pulverized coal at high heat-liberation rates in air-cooled sheet-metal combustors is entirely feasible. Much of the technique which has been evolved for design and comparison of aircraft-type liquid-fuel-burning combustors is applicable to combustors burning pulverized coal. Among the important differences in design is the necessity of avoiding all impingement of pulverized coal on hot metal surfaces, and the comparatively low heat-liberation rates which must be used to provide sufficient time for good combustion of slow-burning carbon particles [200,000 to 500,000 Btu per (cu ft) (hr) (atmosphere), compared to perhaps 5,000,000 Btu per (cu ft) (hr)(atmosphere) for liquid fuels].

Combustor No. 2 was a jet-engine combustor designed for burning kerosene over an extreme range of firing rates. This wide-range performance is due to arrangement of flame-tube perforations to cause strong recirculation of flame into the incoming fuel. This recirculation was also probably responsible for the excellent ignition characteristics of this combustor.

Combustors Nos. 3 and 4 both incorporated a burner admitting a fixed fraction of the total air at the head of the flame tube and were limited in their operating range. This was probably a matter of burner design, as the recirculation in the burner zone was different from that in combustor No. 2. The design of combustors Nos. 3 and 4 has the advantage of providing a maximum residence time per unit of combustor volume, which, in large combustors, should result in high combustion efficiencies.

The principal value of small-scale low-pressure combustion studies appears to lie in comparison of such characteristics as ignition, combustion, cooling of metal parts, temperature distribution at the combustor outlet, and deposition of coke and ash for various combustor configurations. At the present state of the art of combustor design, full-scale work over the complete range of gas-turbine conditions from idling to maximum load, including starting acceleration, and deceleration conditions, must be relied upon for accurate determination of performance characteristics of the final design of combustor. These are especially necessary for investigation of actual gas temperatures and metal temperatures, which may be higher than those in small combustors, and to determine practical means necessary to prevent slag and ash accumulation.

Instrument-Gear Standards and Design

By G. W. KUNTNY,[1] PHILADELPHIA, PA.

Common gear formulas alone do not guarantee smooth, continuous, and uniform gear motion. Refinements and corrections on basic dimensions are sometimes needed. Small pinions, for example, must be made oversize with increased pitch diameters if weak undercut teeth and loss of overlapping tooth action are to be avoided. Accurate mathematical analysis of gear problems can be made by methods developed through the new science of gearing, "involute trigonometry." Graphic gear analysis can be used to visualize gear theory and to double-check mathematical analysis. A fairly accurate graphic check can be made of essential gear elements such as overlapping tooth action, backlash, tolerances, and possible interference by duplicating the action of a gear-hobbing machine on a simple fixture described in this paper. Because accurate gear calculations are complex, the establishment of preselected standard specifications is recommended for frequently used classes and grades of gears. Samples of such "quick-reference" tables are included. They are intended as a timesaver for the busy designer, and as a yardstick of gear quality for the less experienced draftsman.

NOMENCLATURE

The following nomenclature is used in the paper:

A = undercut radius on gear meshing with basic rack having sharp-cornered teeth (see Fig. 2)
A_1 = undercut radius on gear meshing with basic rack having rounded teeth (see Fig. 2)
a = standard addendum
e = error producing undercut or interference
f = radius on tip of tooth
h_t = whole depth of tooth
P = diametral pitch
Q = radius to top of undercut on teeth
r = pitch radius on pinion
r_b = base radius on pinion
x = loss on involute measured from base circle
ϕ = pressure angle

INTRODUCTION

The first requirement in the production of high-quality instrument gears is gear specifications on drawings theoretically correct and complete in every detail. No empirical short-cut method is practical. Neither do simple formulas found in some handbooks give best results. Essential elements are frequently overlooked and valuable gear properties lost by oversimplifying the problem. A modern gear-tooth profile is an involute curve similar to a uniform-motion cam. In a well-designed gear drive having sufficient overlapping tooth action, four cam-shaped tooth profiles, and sometimes as many as six, are normally in action at the same time. The relations of several tooth profiles in action cannot be expressed in simple mathematics. They can, however, be expressed accurately and evaluated through the new science of "involute trigonometry," also known as "involutometry."

The busy designer is handicapped by having to make long time-consuming analytic calculations for gears, which represent only a relatively small part of his project. The economical and efficient procedure is to provide him with preselected standard gear specifications from which he can select gears quickly for a given purpose. Proposed preselected standard gear specifications have been developed in this investigation for the nineteen quality classes of commercial and precision spur gears as recognized by the American Gear Manufacturers Association. Sample pages are shown in Tables 1 to 3 of this paper. Such tables become a timesaver for the busy designer and serve as a yardstick of gear quality for the less experienced draftsman.

This investigation was limited to external spur gears with 20 diametral pitch and finer, although most of the findings apply to other types of gears as well. The emphasis was placed on the requirements of the gear user rather than on those of the gear manufacturer. The practical result desired was the establishment of a detailed standard procedure and reliable data for writing instrument-gear specifications which would guarantee, at reasonable cost, the functional requirements for industrial instruments.

FACTORS AFFECTING GEAR QUALITY

Gear performance is sensitive to the slightest errors in design and workmanship. Slight tooth-profile errors or variations in tooth thickness, small errors in tooth spacing, and surface defects on teeth such as nicks, burrs, and sharp corners, may add up to a noisy gear drive which reduces the usefulness and salability of an instrument. More serious errors, such as excessive undercuts on teeth, too generous tolerances, and large eccentricity or run-out, may impair seriously the operation of an instrument. Suitable material and proper heat-treatment for good wearing qualities are also essential.

A pair of gears must have overlapping tooth action and preferably full involute action between tooth profiles. The proper running clearance, known as "backlash," must be selected carefully for a particular application, excessive speeds and loads avoided, the right type of gear used, tooth profiles selected for minimum sliding between teeth in order to reduce friction losses, proper lubrication and protection against dirt provided, and good engineering principles observed in general.

The efficiency of a gear drive is the final measure of instrument-gear quality. The forces available in instruments often approach zero. If gears consume more than their share of available power, the measurement or control response may fall below the high degree of sensitivity expected from a good instrument.

WHY FORMULAS FAIL

When a designer is faced with a critical gear problem, he usually relies on his favorite handbook, although it may be out-of-date. He calculates pitch, diameters, addendum, depth of tooth, blank sizes, and the like, by the simple formulas given, without realizing the limitations of some of them. Some handbooks fail to note that these simple formulas, like many engineering formulas, give correct values only within certain

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[1] Engineering Department, The Brown Instrument Company. Mem. ASME.

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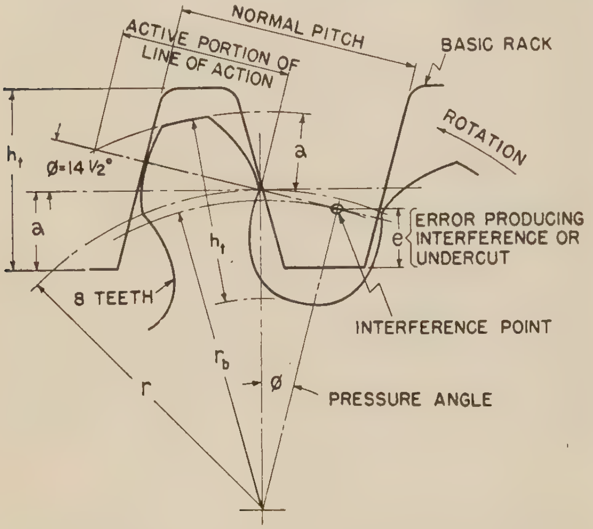
NOTE: Statements and opinions advanced in papers are to be understood as individual expressions of their authors and not those of the Society.

limits. The common gear formulas, for example, give correct diameters for 32 and more teeth only when $14^1/_2$ deg pressure angle is used, and for 18 or more teeth with 20 deg pressure angle. Some handbooks and gear catalogs do not mention the fact that defective tooth profiles develop when the number of teeth or pressure angle is too low. For small gears, for example, certain corrections must be made on some dimensions calculated by the common gear formulas if an efficient gear drive is to be obtained. These required corrections are examined in detail.

Destruction of Overlapping Tooth Action by Excessive Undercuts

Fig. 1 shows the geometrical relationship of error *e* which is responsible for the undercut and the loss of involute on tooth profiles. The error *e* is the distance by which the top land of the basic rack extends toward the gear center beyond the so-called "interference point." While this gear construction satisfies the common gear formulas listed underneath the diagram, it violates the so-called "rule of minimum approach," which in this case overrules the basic formulas. The rule of minimum approach states that a line drawn through the top land of teeth on a basic rack, or the outside radius of the mating gear, must not approach the other gear closer than the interference point. In other words, the error *e* must be zero.



$$r=\frac{1}{2}\frac{n}{P}, \quad r_b=r\cdot\cos\phi, \quad a=\frac{1}{P}$$

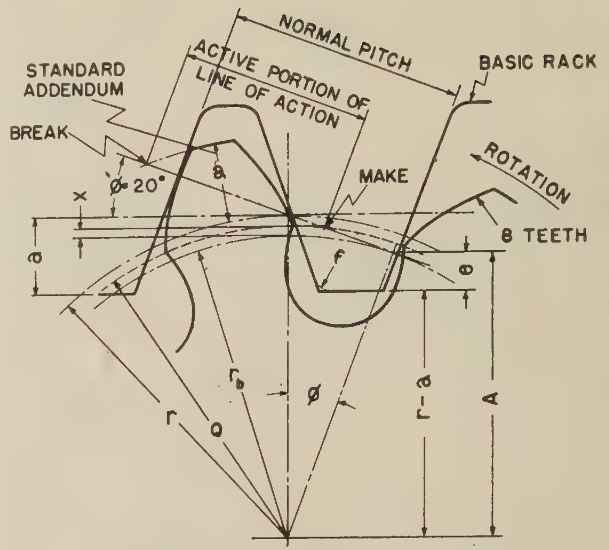
$$h_t\text{(30 PITCH AND FINER)}=\frac{2.200}{P}+.002$$

$$h_t\text{(29 PITCH AND COARSER)}=\frac{2.157}{P}$$

Fig. 1 Defective $14^1/_2$-Deg Involute Pinion With Standard Addendum

It may be suggested that a simple way to eliminate this trouble would be to reduce the length of the mating tooth by the amount *e*. This, however, may mean correcting one error by introducing a new error which also destroys overlapping tooth action. In this particular example, illustrated in Fig. 1, the active portion of line of action would be only approximately the same length as the normal pitch, while it should be at least 120 to 140 per cent of the normal pitch, in order to obtain continuous and uniform gear motion.

Possible Improvement by Increasing Pressure Angle



$$A=r\cdot\cos^2\phi \text{ (TEETH WITH SHARP CORNERS)}$$

$$A_1=r\cdot\cos^2\phi-f \text{ (ROUNDED TEETH)}$$

$$e=A-(r-a),\quad Q=r_b+x,\quad x=\frac{e^2}{6r_b\sin\phi}$$

$$x=\frac{2.7448\,e^2}{r} \text{ FOR } 14\tfrac{1}{2}° \text{ PRESSURE ANGLE}$$

$$x=\frac{1.5158\,e^2}{r} \text{ FOR } 20° \text{ PRESSURE ANGLE}$$

Fig. 2 Defective 20-Deg Involute Pinion With Standard Addendum

Fig. 2 shows the slight improvement possible through increasing the pressure from $14^1/_2$ to 20 deg. A lack of overlapping tooth action still exists, however, and the error *e* is still present. The length of the active portion of line of action in this example is less than the normal pitch. The length of the active portion of line of action can be estimated by finding the loss of involute *x*, with formulas listed below the diagram. Then by adding *x* to the base radius r_b, the radius *Q* to the top of the undercut is obtained. The point where the radius *Q* cuts the line of action marked "make" is the beginning of tooth contact, and the point where the outside radius cuts the line of action marked "break" is the end of tooth contact. The length of tooth contact, called "active portion of line of action" can be measured from the layout. The ratio between active portion of line of action and normal pitch is called "contact ratio," which should be at least 1.2 to 1.4 for obtaining sufficient overlapping tooth action.

Recommendations for Obtaining Full Involute Action

Fig. 3 illustrates the recommendations of the American Standards Association for eliminating undercuts on gear teeth, and for obtaining full involute action on an eight-tooth pinion, by means of long addendum teeth. The defective tooth profiles shown in Figs. 1 and 2 are eliminated by simply increasing the diameter of the gear blank and then generating the teeth with standard tools to standard depths measured from the enlarged outside diameter of blank. The increment which must be added to the nominal outside diameter in order to eliminate undercuts on small pinions has been standardized by the American Standards Association in its Standard B6.1—1932, and by The American Gear Manufacturers Association in its Tentative Standard 207.01—Feb., 1944. The use of long-addendump inions provides the theoretical maximum length of overlapping tooth action. The contact ratio for the eight-tooth long-addendum pinion shown is approximately 1.3, which is satisfactory for most applications.

Oversize long-addendum pinions introduce the slight complications that they require increased gear centers or undersize mating gears. It is common practice to increase the nominal gear centers, or decrease radii of the mating gear, the same amount by which the pinion radii have been increased. These corrections on gear centers or mating gears are, however, an approximation. If a very accurate control of backlash is needed, the theoretical center distance and backlash must be calcu'ated by involute trigonometry. The principal formulas of this new science of gearing are listed in the American Gear Manufacturer Association's Tentative Standard 207.1-Feb., 1944.

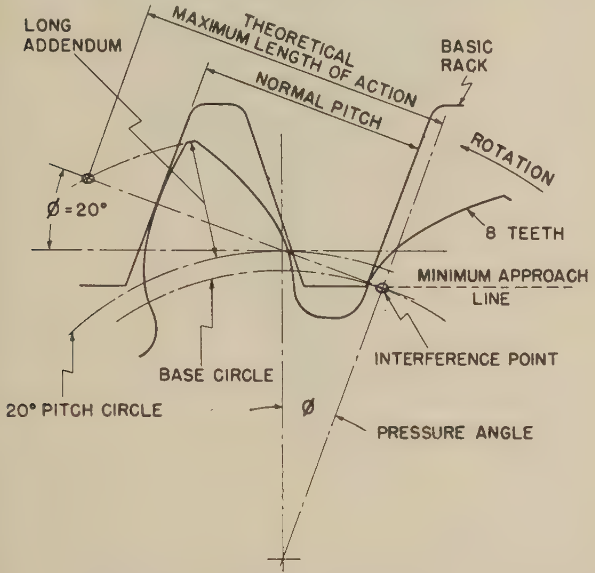


Fig. 3 American Standard 20-Deg Involute Long-Addendum Pinion

The diagram Fig. 3 also illustrates the fact that the eight-tooth standard long-addendum pinion shown is the smallest standard gear having full-depth teeth. Pinions with seven or fewer teeth have reduced tooth depth and, unless the outside diameter is selected properly, have pointed teeth.

Loss of Overlapping Tooth Action Through Cumulative Tolerances and Eccentricity Errors

Even with good tooth profiles it is possible to obtain a defective gear drive, if errors from eccentricity and cumulative tolerances are too large, as illustrated in Figs. 4 and 5. An eight-tooth long-addendum pinion meshing into a basic rack with zero backlash, Fig. 4, has about 30 per cent overlapping tooth action. When, however, the cumulative tolerances on pinion, rack, and mounting dimensions plus minimum backlash allowance should add up to 0.008 on this 48-pitch pinion as shown in Fig. 5, then all overlapping tooth action is lost. Good gearing practice requires that at least 20 to 40 per cent remain under any condition for smooth transfer of power from tooth to tooth.

More complete gear theory can be found in many books available on the subject, of which references (1, 2)[2] are probably most widely known.

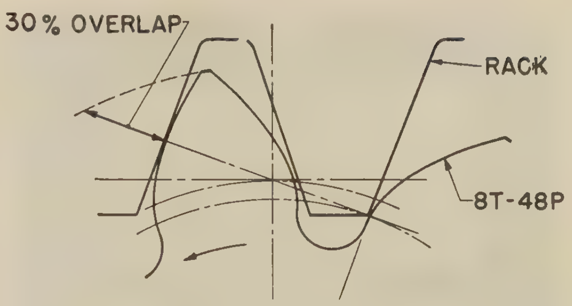


Fig. 4 Maximum Overlapping Tooth Action on Long Addendum Pinion

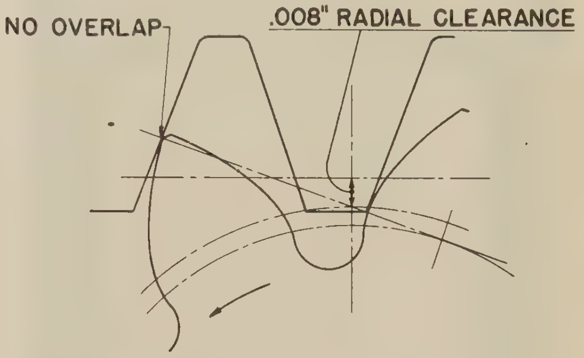


Fig. 5 Loss of Overlapping Tooth Action Through Eccentricity Errors and Cumulative Tolerances

A Rapid Method of Graphic Gear Analysis

A timesaving tool developed for visualizing the complex geometric relationships of various gear elements is illustrated in Fig. 6. This tooth-profile generating fixture duplicates the action of a gear-hobbing machine on paper at 50 to 100 times enlarged scale. While the conventional layout method for developing tooth profiles on a drawing board produces only the normal involute curves, this special fixture also brings out some freak features which may creep in under certain conditions. For a clear understanding of the operating principles of this device, some knowledge of gear-generating methods is desirable. The practical use of this fixture is as follows:

1 An enlarged accurate outline of a few teeth of the gear hob to be used is made on drawing paper and mounted on the cross slide in the center of the fixture as shown.

2 A transparent paper template of a gear blank for a given gear is made on which outside radius, pitch radius, base radius, and root radius are drawn as shown at the right in Fig. 6. The second template shown at the left should be ignored for the present.

3 The paper template of the gear blank is now screwed to a rotating stud which represents the gear center. The adjustable slide of the fixture on which the stud rotates is now moved to the left until the transparent paper template is superimposed on the drawing on the cross slide. The root circle of the gear paper template must be exactly tangent with a straight line drawn along the tip of the hob teeth shown on the cross slide.

4 Equal steps of arbitrary lengths are now marked off along the straight pitch line on the hob teeth on the cross slide and along the pitch circle of the gear blank template, and are numbered as shown in the illustration. We are now ready to generate the tooth profiles shown at the right of the illustration.

5 The cross slide is moved step by step, while the paper template is rotated the same equal steps corresponding with the numbers marked on the cross slide and templates. At each step the outline of the hob teeth is traced on the transparent paper template as shown in light lines on the template. The envelope of the various hob-tooth outlines on the template forms the tooth profile as a gear-hobbing machine would produce it from given dimensions.

6 The tooth profiles of the pinion, shown at the left in Fig. 6, are now generated in the same manner, the cross slide being re-

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[2] Numbers in parentheses refer to the Bibliography at the end of the paper.

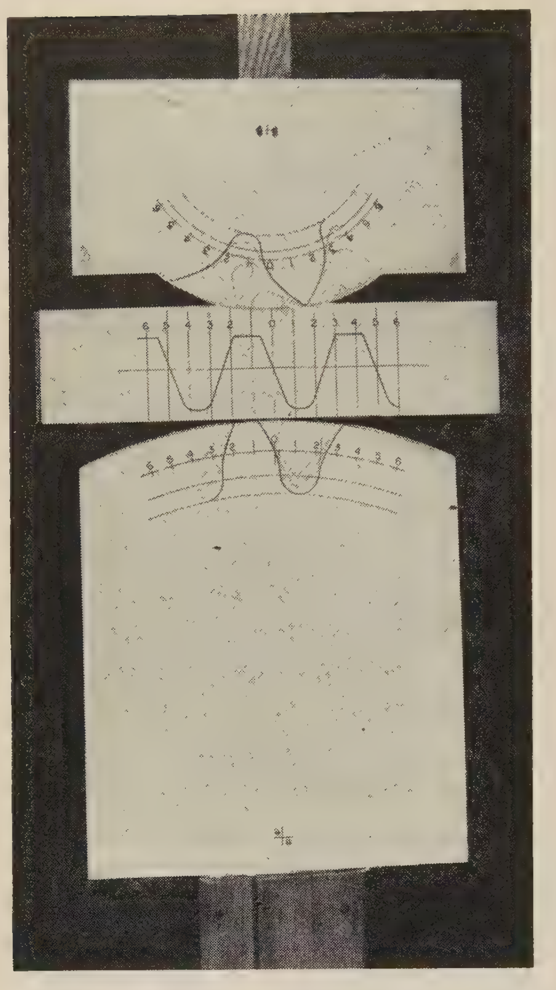


Fig. 6 Fixture for Generating Tooth Profile Templates at Enlarged Scale

versed so that the cutting-edge outline is again used for tracing.

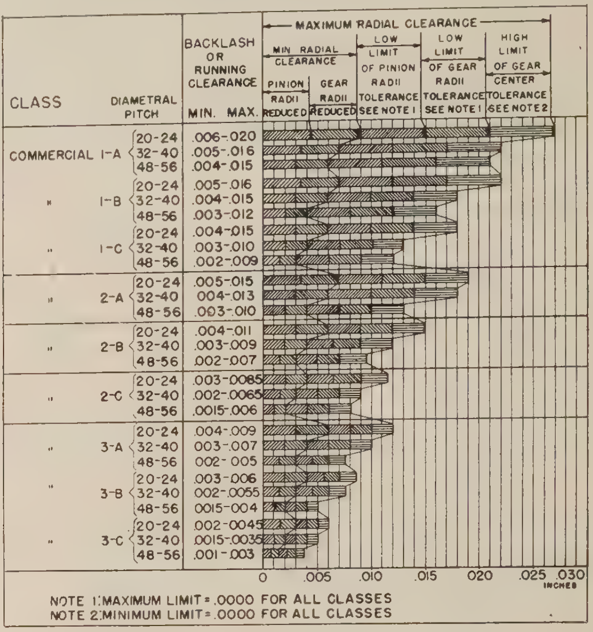
7 The cross slide can now be turned upside down. The two transparent paper templates of gear and pinion are then moved together until the teeth are "in mesh," and one templet is superimposed upon the other. The distance from center to center of the two paper templates should be the same as the theoretical gear centers at enlarged scale.

8 We are now ready to study the pair of gears in motion by rotating both templates together. The essential gear elements, such as overlapping tooth action, backlash, and possible interference between teeth, can be observed and measured fairly accurately at 50 to 100 times enlarged scale. By drawing a line tangent to the two base circles, and intersecting the line of centers, the operating pressure angle can also be measured.

Proposed Basic Specifications

Table 1 is a graphic summary of the proposed basic specifications for nine classes of commercial grade fine-pitch spur gears. Pressure angle of 20 deg was selected according to recommended practice of the American Gear Manufacturers Association. The preferred diametral pitches are 20, 24, 32, 40, 48, and 56; first choices being 32 and 48 diametral pitch. The recommended minimum backlash and maximum backlash vary according to class and pitch from 0.001 in. to 0.020 in. The five elements which determine the minimum and maximum backlash are shown graphically in the block diagram.

Table 1 Proposed Minimum Backlash Allowance Tolerances and Resulting Maximum Backlash for Nine Standard Classes of Commercial Grade 20-Deg Involute Fine-Pitch Spur Gears



CLASS		DIAMETRAL PITCH	BACKLASH OR RUNNING CLEARANCE MIN. MAX.
COMMERCIAL	1-A	20-24	.006-.020
		32-40	.005-.016
		48-56	.004-.015
"	1-B	20-24	.005-.016
		32-40	.004-.015
		48-56	.003-.012
"	1-C	20-24	.004-.015
		32-40	.003-.010
		48-56	.002-.009
"	2-A	20-24	.005-.015
		32-40	004-.013
		48-56	.003-.010
"	2-B	20-24	.004-.011
		32-40	.003-.009
		48-56	.002-.007
"	2-C	20-24	.003-.0085
		32-40	.002-.0065
		48-56	.0015-.006
"	3-A	20-24	.004-.009
		32-40	003-.007
		48-56	002-.005
"	3-B	20-24	.003-.006
		32-40	002-.0055
		48-56	0015-.004
"	3-C	20-24	.002-.0045
		32-40	.0015-.0035
		48-56	.001-.003

NOTE 1: MAXIMUM LIMIT = .0000 FOR ALL CLASSES
NOTE 2: MINIMUM LIMIT = .0000 FOR ALL CLASSES

Minimum backlash is obtained, when both pinion and gear have 18 or more teeth, by reducing the pitch radii of both pinion and gear by the radial minimum backlash allowance indicated in Table 1. When, however, the pinion has 17 or fewer teeth, the total backlash allowance is taken on the larger gear, and no modification for backlash is made on pinions in order to avoid errors on the sensitive tooth profiles of small pinions. In rare cases when both mating gears have 17 or fewer teeth, long-addendum pinions must be used, as given in Table 3, and the minimum backlash allowance must be added to the theoretical center distance.

The maximum backlash of a pair of gears is determined through the cumulative effect of five elements graphically shown in the block diagram of Table 1, including: Minimum backlash allowance on pinion, minimum backlash allowance of gear, tolerances on pinion, tolerances on gears, and tolerances on gear centers.

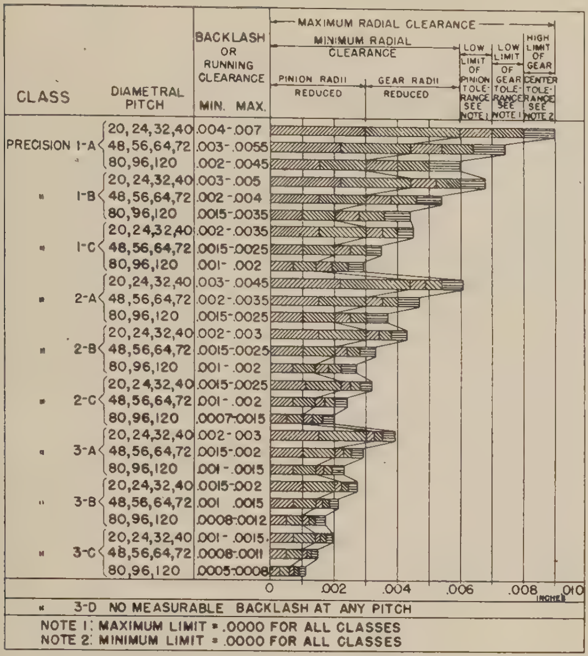
Table 2 is a graphic summary of the proposed basic specifications for ten classes of precision-grade fine-pitch spur gears also based upon recommendations of the American Gear Manufacturers Association. The preferred diametral pitches for precision gears are 20, 24, 32, 40, 48, 56, 64, 72, 80, 96, and 120, first choices being 32, 48, 64, and 80 diametral pitches. The recommended minimum backlash and maximum backlash vary from 0.0005 in. to 0.007 in., according to classes and pitches.

No standard specifications can be given for the highest precision Class 3-D, used for applications in which no measurable backlash is permitted between a pair of gears. Precision-gear specifications are, in general, similar to commercial-gear specifications explained in Table 1, except for smaller backlash allowance, finer tolerances, and better workmanship.

Table 3 is a sample page from a set of "quick reference" tables for designers. From these tables the designer can take directly, without further calculations, all the working dimensions and tolerances as they should be put on shop drawings for the preferred classes and sizes of gears.

The nominal 20-deg pitch radii, listed as r_{nom}, are frequently needed for gear calculation. The actual working radii are usually larger or smaller when allowance for elimination of undercuts or backlash allowance is included.

TABLE 2 PROPOSED MINIMUM BACKLASH ALLOWANCE, TOLERANCES AND RESULTING MAXIMUM BACKLASH FOR TEN STANDARD CLASSES OF PRECISION GRADE 20-DEG INVOLUTE FINE-PITCH SPUR GEARS



CLASS	DIAMETRAL PITCH	BACKLASH OR RUNNING CLEARANCE MIN. MAX.
PRECISION 1-A	20, 24, 32, 40	.004-.007
	48, 56, 64, 72	.003-.0055
	80, 96, 120	.002-.0045
" 1-B	20, 24, 32, 40	.003-.005
	48, 56, 64, 72	.002-.004
	80, 96, 120	.0015-.0035
" 1-C	20, 24, 32, 40	.002-.0035
	48, 56, 64, 72	.0015-.0025
	80, 96, 120	.001-.002
" 2-A	20, 24, 32, 40	.003-.0045
	48, 56, 64, 72	.002-.0035
	80, 96, 120	.0015-.0025
" 2-B	20, 24, 32, 40	.002-.003
	48, 56, 64, 72	.0015-.0025
	80, 96, 120	.001-.002
" 2-C	20, 24, 32, 40	.0015-.0025
	48, 56, 64, 72	.001-.002
	80, 96, 120	.0007-.0015
" 3-A	20, 24, 32, 40	.002-.003
	48, 56, 64, 72	.0015-.002
	80, 96, 120	.001-.0015
" 3-B	20, 24, 32, 40	.0015-.002
	48, 56, 64, 72	.001 .0015
	80, 96, 120	.0008-.0012
" 3-C	20, 24, 32, 40	.001-.0015
	48, 56, 64, 72	.0008-.0011
	80, 96, 120	.0005-.0008

" 3-D NO MEASURABLE BACKLASH AT ANY PITCH

NOTE 1: MAXIMUM LIMIT = .0000 FOR ALL CLASSES

NOTE 2: MINIMUM LIMIT = .0000 FOR ALL CLASSES

MAXIMUM RADIAL CLEARANCE
MINIMUM RADIAL CLEARANCE
PINION RADII REDUCED
GEAR RADII REDUCED
LOW LIMIT OF PINION TOLERANCE SEE NOTE 1
LOW LIMIT OF GEAR TOLERANCE SEE NOTE 1
HIGH LIMIT OF GEAR CENTER TOLERANCE SEE NOTE 2
0
.002
.004
.006
.008
.010
INCHES

The gaging pitch radii listed as r_{gag}, are the actual working dimensions in which all needed corrections are included. This dimension added to the pitch radius of a master gear gives the center distance to which the so-called "run-around" gage must be set for making a composite check on a finished gear.

The outside radii r_o, include allowance for permissible variations in size and runout.

The root radius r_r is a reference dimension for calculating the largest permissible hole in the gear.

The whole depth of tooth h_t, is the amount by which the cutting tool is fed into the gear blank, measured from the outside diameter.

The minimum number of teeth on mating gear N, for each gear listed, and the resulting contact ratio m_p, are needed by designers for checking whether sufficient overlapping tooth action exists for a given application.

The M dimension, listed in the last column of Table 3, permits a very accurate measurement of pitch diameter by means of a micrometer and two precision wires. The measurement can be made while the gear is still on the arbor of the gear-cutting machine. The wire-measurement check can be combined with the composite check on the run-around gage for a double inspection of critical precision gears.

ACKNOWLEDGMENT

The diagrams, tables, and other information in this paper are reproduced with the permission of the sponsor of this investigation, The Brown Instrument Company, a Division of Minneapolis-Honeywell Regulator Company.

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TABLE 3 QUICK-REFERENCE TABLE FOR PROPOSED 48 DIAMETRAL PITCH LONG-ADDENDUM PINIONS, 20-DEG PRESSURE ANGLE, FULL-DEPTH INVOLUTE, COMMERCIAL "GENERAL PURPOSE" CLASS 2-B

Number of teeth on pinion n	Nominal 20 deg pitch radius r_{nom}	Gaging pitch radius +0.000 —0.002 r_{gag}	Outside radius +0.0000 —0.0025 r_0	Root radius r_r	Nominal whole depth of tooth h_t	Minimum number of teeth on mating gear N	Contact ratio, or number of active teeth m_p	Measurement over 0.040 wires M
5 6 7	See section "extra small pinions"							
8	0.08333	0.0941	0.1152	0.0674	0.0478	40	1.31	0.2398
9	0.09375	0.1033	0.1243	0.0765	0.0478	36	1.34	0.2566
10	0.10417	0.1126	0.1336	0.0858	0.0478	33	1.37	0.2800
11	0.11458	0.1218	0.1428	0.0950	0.0478	30	1.39	0.2972
12	0.12500	0.1310	0.1520	0.1042	0.0478	27	1.41	0.3196
13	0.13542	0.1403	0.1611	0.1134	0.0478	25	1.42	0.3371
14	0.14583	0.1495	0.1703	0.1225	0.0478	23	1.43	0.3588
15	0.15625	0.1587	0.1795	0.1317	0.0478	21	1.43	0.3764
16	0.16667	0.1679	0.1887	0.1409	0.0478	19	1.44	0.3976
17	0.17708	0.1772	0.1990	0.1512	0.0478	18	1.44	0.4153

Rule 1: Long addendum pinions, listed on this page, are considered standard for pinions with 17 or fewer teeth. No modifications on dimaters or tooth thickness should be made on Long Addendum Pinions.

Rule 2: The preferred numbers of teeth for gears are *underlined* in tables.

The Removal of Aldehydes From Diesel Exhaust Gas

By R. F. DAVIS[1] and M. A. ELLIOTT,[2] PITTSBURGH, PA.

This report presents the results of studies (*a*) to determine the relation between aldehyde content of Diesel-exhaust gas and the odorous and irritating properties of that gas; (*b*) to determine the effectiveness of different scrubbing media for removing aldehydes from Diesel-exhaust gas. Observations on the odor and irritation produced by Diesel exhaust gas have shown that both of these properties can be correlated with the concentration of aldehydes in the exhaust gas. The threshold concentration for perception of odor is approximately 0.2 to 0.3 ppm of aldehydes (expressed as equivalent formaldehyde). The threshold of nasal and eye irritation occurs at about 1 ppm of aldehydes (expressed as equivalent formaldehyde). A series of full-scale tests on the removal of aldehydes by scrubbing with water showed that, as the concentration of aldehydes in the scrubbing solution increases, the percentage removal of aldehydes decreases. At elevated temperatures, the removal was nil, and under no conditions was complete removal obtained.

From a series of laboratory tests, it appeared that aqueous solution of sodium sulphite might be used in removing aldehydes from Diesel exhaust gas if hydroquinone was added to inhibit the oxidation of sodium sulphite. A full-scale test showed that an aqueous scrubbing solution, containing 10 per cent sodium sulphite by weight and 0.5 per cent hydroquinone, removed substantially all aldehydes for a period of 7 hr, and 90 per cent or more of the aldehydes for a period of 15 hr. In this test approximately 3000 cu ft of dry exhaust gas (at 60 F and 29.92 in. Hg) was scrubbed per hour at a scrubbing temperature of 133 F. Estimates of the cost of scrubbing Diesel exhaust gas indicate that the cost of materials would be approximately 80 cents for an engine operating continuously for 8 hr and producing an average of 5000 cu ft of dry exhaust gas (at 60 F and 29.92 in. of Hg) per hour.

INTRODUCTION

ODOROUS and irritating materials are present in the exhaust gases from Diesel engines under some operating conditions and with certain types of fuel. In most applications of the Diesel engine, the dilution of exhaust gases with the ambient air is sufficient to reduce the concentration of odorous and irritating materials to a nonobjectionable level. However, the odor problem has been encountered in certain operations of Diesel engines in congested areas, and it becomes of considerable importance when Diesel engines are used in confined spaces, as, for example, in mining and tunneling operations.

The desirability of eliminating or minimizing the odor from Diesel-exhaust gases became apparent in connection with the Bureau of Mines' investigations of the hazards of using Diesel engines underground. In one underground application of Diesel engines on which detailed data are available (1),[3] the characteristic odor of Diesel-exhaust gas was evident even though aldehydes, which are generally regarded as responsible for the odor, were present in the air only in extremely low concentrations. In this application, the odor was considered objectionable by some individuals. In an effort to eliminate such objections to the use of Diesel engines underground, the Bureau of Mines investigated various methods for removing the odors from Diesel-exhaust gases. This report summarizes the results of these studies.

REVIEW OF PREVIOUS WORK

The odor of Diesel-exhaust gas has been mentioned frequently in the technical literature, but very little quantitative data have been published relating odor intensity to a particular constituent of the exhaust gas. Investigators of combustion in the Diesel engine (2) have pointed out that aldehydes and possibly other oxygenated organic compounds and polymerization products are responsible for the odor of Diesel exhaust gas. Other investigators (3, 4) have attributed the odor of Diesel exhaust to sulphur compounds. Such compounds may contribute to odor, but tests by the Bureau of Mines (5) have shown that the odor of Diesel exhaust was evident even with fuels containing essentially no sulphur. In these tests (5), odor intensity and degree of irritation were related to the concentration of aldehydes in the exhaust gas. Subsequently, Nikita, Levin, and Kichline (6) related the odor intensity of the exhaust from gasoline engines to concentration of aldehydes, and Wetmiller and Endsley (7) used aldehyde concentration as a measure of odor intensity of Diesel exhaust gas.

Very little information has been published on methods for deodorizing Diesel exhaust gases. Maurin and Kling (8) showed that water was not effective in deodorizing Diesel exhaust gases, but that scrubbing with aqueous solution of sodium carbonate or lime, followed by passage over activated charcoal was effective. These authors presented only limited quantitative data. Schmidt (4) claims that addition of chloride or activated oxygen to the fuel will eliminate odor from Diesel exhaust gases.

SCOPE OF PRESENT WORK

From the literature survey, it seemed desirable (*a*) to obtain additional quantitative data on the relation between odor intensity and irritating effect of Diesel exhaust gas and the concentration of aldehydes in the exhaust gas; (*b*) to obtain quantitative data on the effectiveness of water as a scrubbing medium; and (*c*) to develop an economical method for removing aldehydes from Diesel exhaust gas. These three objectives define the scope of the work to be described.

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[3] Numbers in parentheses refer to the Bibliography at the end of the paper.

RELATION BETWEEN ODOR AND IRRITATION, AND CONCENTRATION OF ALDEHYDES

Apparatus and Procedure. In determining the relation between the odor intensity and irritating effect of Diesel exhaust gas and the concentration of aldehydes in the exhaust gas, observations were made on the exhaust gas before (raw gas) and after (scrubbed gas) passage through a water scrubber. The details of the scrubbing equipment are not significant in connection with odor tests and are given in a subsequent section of this report.

Exhaust gas was conducted in a 1-in. pipe to an observation station. The observation station was a closed chamber 1 ft × 1 ft × $2^1/_2$ ft, constructed of wood and having a front door hinged at the top. Exhaust gas was passed continuously through the observation chamber with the door closed. The door was opened only when an observation was made. Observations of odor intensity and nasal irritation were based on one inhalation. Observations of eye irritation were based upon an exposure of 5 to 10 sec. At least 5 min elapsed between observations of any individual. The observer did not know the concentration of aldehyde in the exhaust gases nor did he know whether the observations were made on raw or scrubbed gas.

Aldehydes were determined by the method used by the American Gas Association (9), except that the silver was dissolved in hot 1:3 nitric acid and refiltered to obtain the final filtrate. This method determines total aldehydes present, but the results are reported as concentration of equivalent formaldehyde in parts per million parts by volume.

Odor intensity and nasal and eye irritation were evaluated in accordance with the following scale (10):

	Odor Intensity		Eye and Nasal Irritation
0	No odor	0	No irritation
1	Very faint, minimum odor, but positively perceptible	1	Faint, just perceptible, threshold, not painful
2	Faint, weak odor, readily perceptible	2	Moderate
3	Easily noticeable, moderate intensity	3	Strong, discomforting, painful, but may be endured
4	Strong, cogent, forcible odor	4	Intolerable, cannot be endured
5	Very strong, intense effect, may bite or irritate		

EXPERIMENTAL RESULTS

The results of odor-intensity observations are shown in relation to concentration of aldehydes in the exhaust gas in Fig. 1. Similar correlations are shown for the intensity of nasal and eye irritation in Figs. 2 and 3, respectively. In these figures the sense reaction is plotted as a function of the logarithm of the concentration of aldehydes. This functional relationship expresses Weber's law (11, 12), which states that the sense reaction is proportional to the logarithm of the stimulus. Gamble (13) demonstrated that Weber's law applies to the sense of smell, and Katz and Talbert (10) corroborated this and showed also that it applied to nasal and eye irritation.

Fig. 1 shows that the odor intensity of Diesel exhaust gas is related to concentration of aldehydes. Throughout the range of concentrations covered, the relation is linear, indicating that Weber's law applies. The same conclusions apply to nasal and eye irritation although the dispersion of the observations on eye irritation is greater than that of the other sense reactions. Each point in Figs. 1, 2, and 3 represents an average of the observations between five and eleven different individuals. Even when this comparatively large number of observations is used to obtain an average index of the sense reaction, the average points deviate approximately ±0.5 units from the best linear relation. In spite of this, the curves indicate a definite trend of sense reaction with aldehyde concentration. Furthermore, removal of aldehydes by water-scrubbing decreased odor and irritation. From these results it was concluded that aldehydes could be used as a satisfactory criterion of odor and irritation and that the most promising method for elimination of odor and irritation would involve removing of aldehydes from the exhaust gas.

Extrapolation of the relations, Figs. 1, 2, and 3, shows that the threshold of odor occurs at an aldehyde concentration of approximately 0.2 to 0.3 ppm by volume, and that the threshold of nasal and eye irritation occurs at a concentration of about 1 ppm.

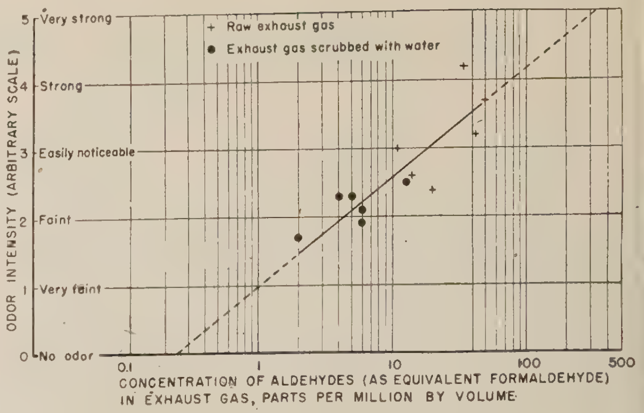

FIG. 1 EFFECT OF ALDEHYDE CONCENTRATION ON ODOR INTENSITY OF DIESEL EXHAUST GAS

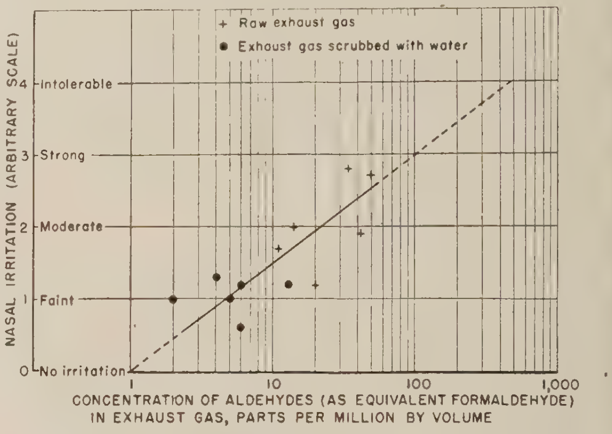

FIG. 2 EFFECT OF ALDEHYDE CONCENTRATION ON NASAL IRRITATION FROM DIESEL EXHAUST GAS

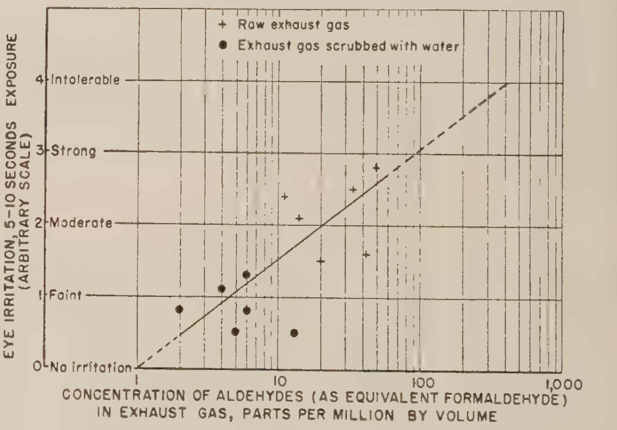

FIG. 3 EFFECT OF ALDEHYDE CONCENTRATION ON EYE IRRITATION FROM DIESEL EXHAUST GAS

Effect of Scrubbing With Water on Removal of Aldehydes

The use of water as a scrubbing medium for removing aldehydes from Diesel-exhaust gas has been mentioned frequently in both the technical and trade literature. Theoretical considerations indicate that incomplete removal of aldehydes is likely unless the gas is scrubbed countercurrently with fresh water containing no dissolved aldehydes. Such a scrubbing system is not feasible for mobile Diesel-powered equipment. Even though scrubbing with water did not appear to be attractive, it was considered advisable to obtain quantitative data on the limitations of water as a scrubbing medium for removing aldehydes from Diesel exhaust gases, because of the number of inquiries on this subject received by the Bureau of Mines.

Full-scale tests were made in which the exhaust gases from a standard commercial 4-stroke-cycle Diesel engine were scrubbed with water in a bubbling-type scrubber. A schematic outline of the equipment is shown in Fig. 4.

A bubbling-type scrubber was used in these tests because of the simplicity of its construction, and because this type scrubber had been used on Diesel mine locomotives (1, 14). The scrubber was 18 in. × 18 in. × 18 in. and contained 10 gal of water under operating conditions. The exhaust gases entered through a 4-in. pipe, Fig. 4. The submerged section of this pipe was parallel to the bottom of the scrubber and contained five 1-in-diam holes on each side. The holes were drilled on 2-in. centers longitudinally. The longitudinal center lines on each side of the pipe were at an angle of 45 deg from the vertical (see Fig. 4). The scrubber contained a baffle plate and a cyclone separator to minimize entrainment. After leaving the scrubber, the gases passed through a packed tower to remove traces of entrained water which might have interfered with the determination of aldehydes in the outlet gases.

In making a test, the engine-operating conditions were adjusted during the first hour of operation. These conditions were then maintained for the duration of the test (approximately 6 hr). During this period, the water lost from the scrubber in saturating the exhaust gases was replenished by fresh water to maintain approximately 10 gal of water in the scrubber at all times. Samples of the exhaust gas at the inlet and outlet of the scrubber were taken at intervals during the test. These samples were analyzed for aldehydes, as mentioned previously, and for oxides of nitrogen, carbon dioxide, oxygen, carbon monoxide, methane, hydrogen, and nitrogen by methods described elsewhere (5). Samples of the scrubbing water were taken also at periodic intervals and analyzed for aldehydes.

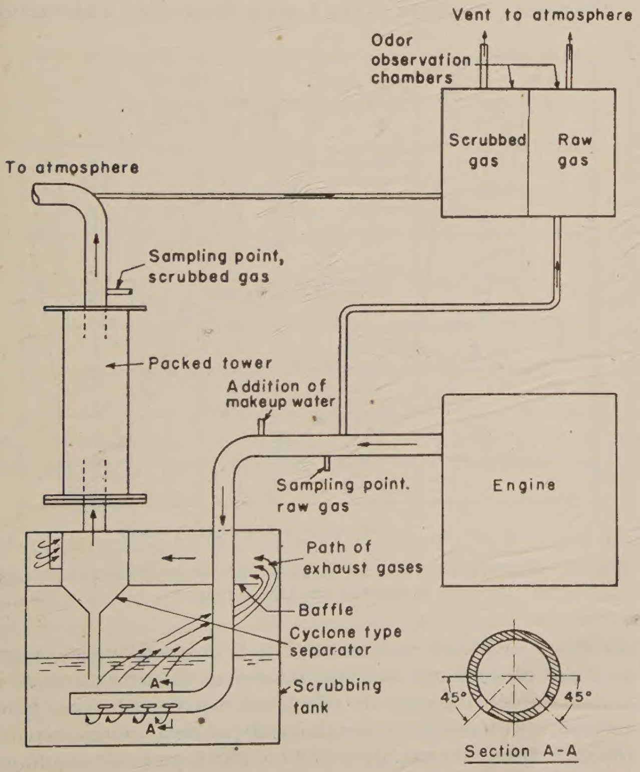

Fig. 4 Schematic Representation of Scrubbing System for Removing Aldehydes From Diesel Exhaust Gas

The injectors and the fuel pump in the engine used in these tests were not in proper mechanical condition, and for this reason, aldehyde concentrations in the exhaust were higher than with a properly operating engine. This was an advantage in these tests because a relatively wide range of aldehyde concentrations was desired in the odor tests previously described.

The results of a typical test are shown in Fig. 5. In this test the concentration of aldehydes in the inlet gas ranged from 44 to 60 ppm, and that in the outlet gas ranged from 28 to 38 ppm. As the test progressed, the concentration of aldehydes in the scrubbing water increased, and the per cent removal of aldehydes decreased from about 50 at the beginning of the test to 14 at the end. The same trend was observed in all tests in which water was used as a scrubbing medium.

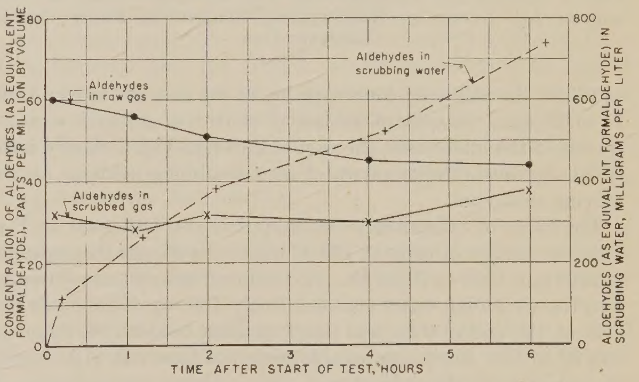

Fig. 5 Variation With Time of Concentration of Aldehydes in Raw Gas, Scrubbed Gas, and Scrubbing Water

In scrubbing Diesel-exhaust gases, the temperature of the scrubbing solution depends on the temperature of the exhaust gases entering and on the fuel:air ratio at which the engine is operating. Under actual operating conditions, the temperature in the scrubber will range from approximately 80 to 160 F. Therefore the effect of temperature on aldehyde removal was examined and illustrated results are shown in Fig. 6. To compare the results, the percentage of aldehydes removed is shown as a function of the concentration of aldehydes in the scrubbing water. Fig. 6 shows that at any given temperature, the percentage of removal decreases as the concentration of aldehydes in the scrubbing water increases. The figure also shows that at any given concentration of aldehydes in the scrubbing water, the percentage of removal decreases markedly as the temperature of the scrubbing water increases.

The data presented in Fig. 6 are not rigorously comparable because the concentration of aldehydes in the raw gas was not the same in every test. In the tests at an exhaust-gas throughput of 4500 cu ft per hr, the range of concentration was as follows: 75 to 134 ppm in the test at 103 F; 44 to 60 ppm in the test at 122 F; and 16 to 29 ppm in the test at 140 F. In the test at an exhaust-gas throughput of 2100 cu ft per hr, and a scrubbing temperature

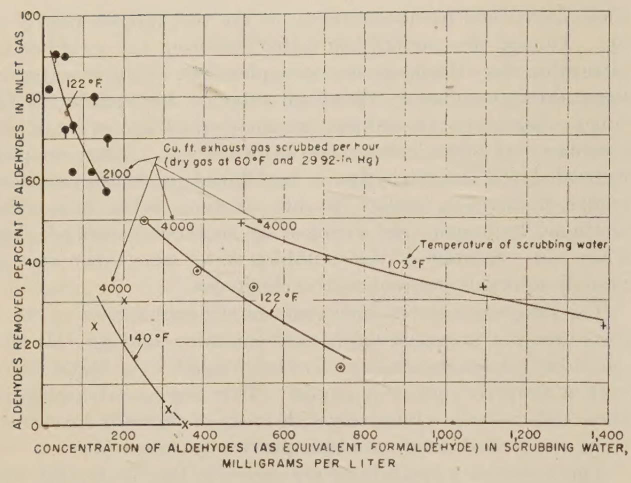

Fig. 6 Effect of Temperature and Concentration of Dissolved Aldehydes on Removal of Aldehydes From Diesel Exhaust Gas

of 122 F, the aldehyde concentration in the raw gas ranged from 11 to 42 ppm. In spite of the lack of control of aldehyde concentration in the inlet gases, the results shown in Fig. 6 clearly indicated the unsuitability of water as a scrubbing medium for removing aldehydes.

The effect of exhaust-gas throughput is also indicated in Fig. 6 by the results of tests at 122 F with exhaust-gas throughputs of 2100 and 4500 cu ft per hr. At the lower exhaust-gas throughput, the scrubbing water contained only 180 mg of aldehyde per liter at the end of 6 hr, and the percentage of aldehyde removed was 60 to 70. For a comparable period of time but with double the exhaust-gas throughput and with a higher concentration of aldehydes in the raw gas, the scrubbing water contained 740 mg of aldehydes per liter, and the percentage of removal was only 14.

Water scrubbing was effective in reducing the odor and irritation of Diesel exhaust gas to the extent that it removed aldehydes from the gas. In every instance in which significant proportions of aldehydes were removed, the intensity of odor and irritation was decreased. In general, the decrease ranged from 0.5 to 1.5 units on the arbitrary sense-reaction scale described previously. In no test was the scrubbed gas odorless or nonirritating, see Figs. 1 to 3.

Removal of Aldehydes by Aqueous Sodium-Sulphite Solutions

In view of the foregoing results with water as a scrubbing medium, it is evident that some other means must be employed if substantially complete removal of aldehydes from Diesel exhaust gas is to be realized. A survey of the literature disclosed several possible chemical reactions which might be utilized in removing aldehydes. Each of these was investigated on a laboratory scale by passing air-containing formaldehyde through the solution in question and determining the formaldehyde removal. The two most effective reactions studied were (*a*) oxidation of formaldehyde by chromic-acid solution; and (*b*) reaction with aqueous solution of sodium sulphite. The latter method appeared to be more suitable for use in Diesel engines because corrosion and handling problems would be less troublesome than with chromic-acid solutions.

The laboratory experiments on the removal of formaldehyde by the reaction

$$Na_2SO_3 + HCHO + H_2O \longrightarrow NaOH + CH_2\,(NaSO_3)\,OH$$

showed that removal of 50 ppm of formaldehyde from air was substantially complete for long periods of time at temperatures up to 160 F, and with solutions containing 2 to 5 per cent by weight of sodium sulphite. These tests showed also that the removal of formaldehyde decreased markedly when most of the sodium sulphite had been oxidized to sodium sulphate by the oxygen in the air. Since Diesel exhaust gases contain significant concentrations of oxygen, it is necessary to inhibit or retard the oxidation of sodium sulphite to extend the effective life of the scrubbing solution. Previous work (15) had shown that hydroquinone was the most effective inhibitor for oxidation of sodium sulphite. Under the conditions of the laboratory-scale tests at 160 F, the addition of 0.3 per cent hydroquinone to a 5 per cent sodium-sulphite solution retarded oxidation significantly. For example, at the end of 5 hr, the concentration of sodium sulphite was 3.1 per cent without inhibitor, and 3.9 per cent with inhibitor.

To determine the effectiveness of aqueous sodium-sulphite solutions in removal of aldehydes from Diesel exhaust gas under actual operating conditions, a series of full-scale tests were made using the apparatus previously described in discussing scrubbing with water.

The first full-scale tests were made with no inhibitor added to the solution to determine whether oxidation of sulphite would be a problem under practical operating conditions, and to determine whether loss of activity of the solution resulting from oxidation might be obviated by using higher concentrations of sodium sulphite. The results of these tests are shown in Fig. 7. It will be observed that solutions containing 5 per cent sodium sulphite became inactive in less than 1 hr. The 10 per cent solution was active for about 2 to 3 hr, and the 20 per cent solution for about 5 to 6 hr. The tests with the 20 per cent solution were run at two engine loads, namely, idling (scrubbing-water temperature about 100 F), and 50 per cent load (scrubbing-water temperature about 130 F). Fig. 7 shows that the scrubbing solution was more effective at the lower scrubbing temperature.

The results, presented in Fig. 7, show clearly that under actual operating conditions, sodium sulphite is oxidized by the oxygen in Diesel exhaust gas and that increasing the concentration of sodium sulphite increases the effective life of the solution. However, even with solutions containing 20 per cent sodium sulphite, the maximum life was only 5 to 6 hr, which probably would not be satisfactory for a practical application.

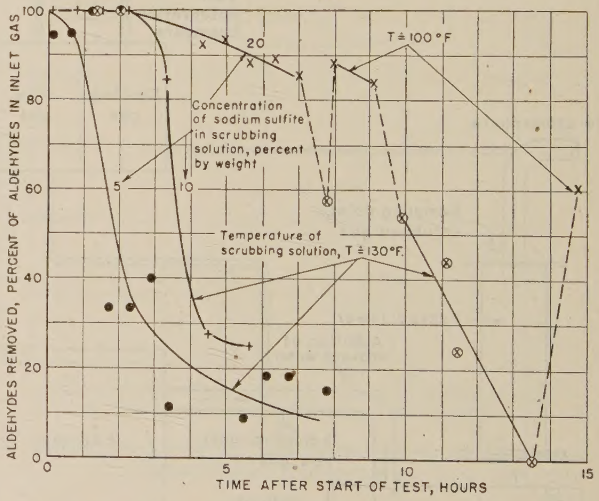

Fig. 7 Effect of Concentration of Sodium Sulphite on Removal of Aldehydes

The foregoing results indicated the desirability of using an inhibitor to increase the effective life of the scrubbing solution. Accordingly, a series of full-scale tests were made with different concentrations of hydroquinone added to a 10 per cent solution of sodium sulphite. The results of these tests are presented in Fig. 8. This figure shows that additions of hydroquinone have a marked influence in extending the effective life of the scrubbing solution. For example, with no inhibitor, the solution was inactive after approximately 3 hr, whereas, with a solution containing 0.5 per cent hydroquinone, the activity was acceptable for periods up to 12 to 15 hr. The variation of scrubber inlet and outlet aldehyde concentration with time in the test with 0.5 per cent hydroquinone present is shown in Fig. 9. Removal of aldehydes was substantially complete for 7 hr of continuous operation in this test. The three periods of highest inlet aldehyde concentration occurred when the engine was idled at the beginning and end of a test period.

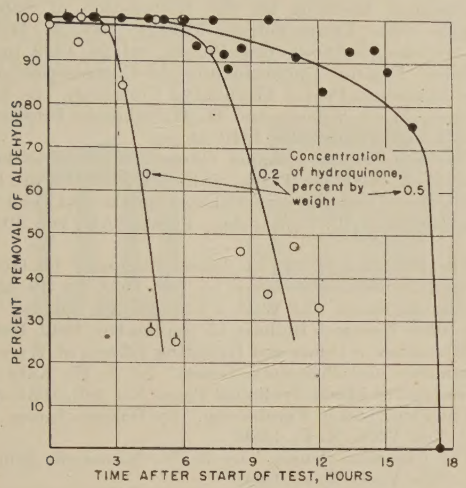

FIG. 8 EFFECT OF INHIBITOR ON REMOVAL OF ALDEHYDES FROM DIESEL EXHAUST GAS BY 10 PER CENT SODIUM-SULPHITE SOLUTIONS
(Temperature of scrubber 133 F.)

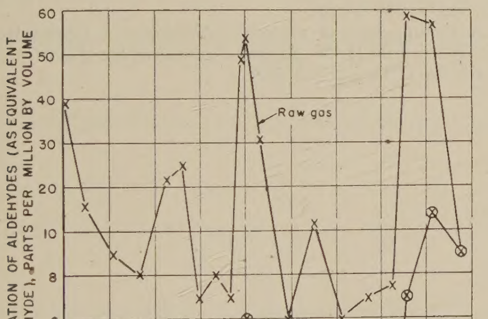

FIG. 9 VARIATION OF ALDEHYDE CONCENTRATION IN RAW AND SCRUBBED GAS WITH TIME IN TEST WITH INHIBITED SODIUM-SULPHITE SOLUTIONS

Test operators made observations of odor, and when aldehyde removal was substantially complete these operators reported that the scrubbed exhaust gases were substantially odorless. In the test with 0.5 per cent hydroquinone present (see Fig. 9), three impartial observers had no difficulty in distinguishing between scrubbed and unscrubbed gas. These observers reported comparatively little odor and irritation in the scrubbed gas.

Sodium-sulphite solution removed small quantities of carbon dioxide, but carbon monoxide and oxides of nitrogen were not removed.

PRACTICAL CONSIDERATIONS IN REMOVING ALDEHYDES FROM DIESEL-EXHAUST GAS

The application of the foregoing results to the removal of aldehydes from the exhaust of a Diesel-powered mobile unit would involve: (*a*) the installation of a suitable scrubber; (*b*) the installation of an auxiliary tank containing either water or scrubbing solution; and (*c*) the provision of an automatic means for replenishing the water lost by evaporation either with water or scrubbing solution from the auxiliary tank. Such equipment has been installed in European Diesel mine locomotives in which the exhaust gases are passed through water scrubbers to reduce temperatures and quench flame or sparks.

If a scrubbing system were installed to remove aldehydes from Diesel exhaust gas, the system should be designed so that it would be effective in removing aldehydes for some selected period of time. In the case of the mine locomotive, this might be 8 hr, which is the duration of one shift. At the end of this time the spent scrubbing solution would be discharged and the system replenished with fresh solution.

It is not possible to estimate accurately the cost of removing aldehydes from Diesel exhaust gases until detailed information is available on the engine operating conditions in any particular situation. However, the cost can be approximated from the results of the test with 0.5 per cent hydroquinone added to a 10 per cent sodium-sulphite solution. Ten gallons of this solution removed 90 per cent or more of the aldehydes from Diesel exhaust gas for about 15 hr at a temperature of 133 F, and with inlet aldehyde concentrations of 30 ppm or less. During the period, approximately 45,000 cu ft of dry exhaust gas (corrected to 60 F and 29.92 in. Hg) was scrubbed. The oxygen content of the exhaust gas was 13.5 per cent. If we assume, as the results indicate, that oxidation of the sodium sulphite is the factor that limits the life of the solution, then the cost of the chemicals used for scrubbing will be determined by the total volume of exhaust gas that can be passed through the solution before it becomes inactive. The foregoing results permit such an estimate to be made as follows:

Basis, 10 gal (approximately 91 lb of scrubbing solution)	
9.1 lb of sodium sulphite at $0.0525 per lb	$0.48
0.45 lb of hydroquinone at $0.90 per lb	0.41
Total	$0.89

Cost per M cu ft of dry exhaust gas at 60 F and 29.92 in. Hg = 89/45 = 2 cents

If it is assumed that an engine produces an average of 5000 cu ft of dry exhaust gas per hr and operates continuously for 8 hr a day, the daily cost for scrubbing chemicals would be $0.80, and the scrubbing system should be designed for a solution capacity of approximately 9 gal. The foregoing estimates are only approximate, but they do furnish an indication of the order of magnitude of the cost of removing aldehydes by scrubbing the exhaust gas with aqueous sodium sulphite solutions.

SUMMARY AND CONCLUSIONS

This report presents the results of studies (*a*) to determine the relation between aldehyde content of Diesel-exhaust gas and the odorous and irritating properties of that gas; (*b*) to determine the effectiveness of different scrubbing media for removing aldehydes from Diesel exhaust gas.

Observations on the odor and irritation produced by Diesel exhaust gas have shown that both of these properties can be correlated with the concentration of aldehydes in the exhaust gas. The threshold concentration for perception of odor is approximately 0.2 to 0.3 ppm of aldehydes (expressed as equivalent formaldehyde). The threshold of nasal and eye irritation occurs at about 1 ppm of aldehydes (expressed as equivalent formaldehyde).

A series of full-scale tests in the removal of aldehydes by scrubbing with water showed that as the concentration of aldehydes in the scrubbing solution increases, the percentage removal of aldehydes decreases. At elevated temperatures, the removal was nil, and under no conditions was complete removal obtained.

From a series of laboratory tests, it appeared that aqueous solution of sodium sulphite might be used in removing aldehydes from Diesel exhaust gas if hydroquinone was added to inhibit the oxidation of sodium sulphite. A full-scale test showed that an aqueous scrubbing solution, containing 10 per cent sodium sulphite by weight and 0.5 per cent hydroquinone, removed substantially all aldehydes for a period of 7 hr, and 90 per cent or more of the aldehydes for a period of 15 hr. In this test, approximately 3000 cu ft of dry exhaust gas (at 60 F and 29.92 in. Hg) was scrubbed per hour at a scrubbing temperature of 133 F. Estimates of the cost of scrubbing Diesel exhaust gas indicate that the cost of materials would be approximately 80 cents for an engine operating continuously for 8 hr and producing an average of 5000 cu ft of dry exhaust gas (at 60 F and 29.92 in. Hg) per hour.

ACKNOWLEDGMENTS

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